International Journal of Enhanced Research in Science, Technology & Engineering
ISSN: 2319-7463, Vol. 5 Issue 3, March-2016

A Thermodynamic and Kinetic Study for Adsorption of a Number of Dyes from their Aqueous Solutions on a New Kind of Activated Carbon Prepared by Pomegranate (Punica Granatum) Peels via Chemical Treatment

Emad A. S. AL-Hyali[1], Ammar A. H. AL-Khazraji[2], Semaa I. K. AL-Taey[3]

[1,2,3]Department of Chemistry/College of Education of Pure Sciences/University of Mosul/Iraq

ABSTRACT

This research included the preparation of many samples of activated carbon by using pomegranate peels as a raw material through reacting them with different ratios of potassium hydroxide, were about [(1:0.5) - (1:3)] [pomegranate peels:KOH], the increase was 0.5% weight of the basic per reaction at 350C^0, for three hours. Then, the temperature was risen into 550±25C^0 and the heating was going on for two hours. Later on, different mixtures of pomegranate peels, asphalt, resin novolak as well as mixture of (1:1) (Asphalt: Novolak) were added by different ratios that were about (5-25)% weight, the increase was 5% weight of the added per reaction and they were prepared exactly as the previous steps done by using a constant ratio of KOH [1:2.5] [pomegranate peels:KOH] as it is the best ratio used from potassium hydroxide. The efficiency of the activated carbon prepared samples were determined via measuring their characteristics like:[density, ash content, humidity, measuring their efficiency as for iodine adsorption from its aqueous solution as well as using a number of dyes in determining its adsorption- efficiency]; the efficiency of the activated carbon prepared-samples was tested by making a thermodynamic and kinetic study of using the adsorbent prepared. This study was conducted at initial concentrations of the two dyes 2×10^{-4}M, the contact time was (5-70)min. and the temperatures were at(15- 55)C^0. The thermodynamic functions (ΔG^0, ΔH and ΔS^0) were calculated by depending on the results of temperatures- effect. The results got have indicated that the dyes adsorption under study happens spontaneously towards the connection on the surface which is an exothermic process and controlled by physical powers lead finally to reducing the randomness of the adsorption system.

Also, this research included the application of Freundlich, Langmuir and Tempkin isotherms on the experimental data for adsorption, the results showed that Freundlich isotherm was more applying on the studied system. In kinetic study, the equations of the pseudo first order and second order, Elovich equation and the intra particle diffusion were applied on the experimental data for the adsorption, the results showed that the adsorption system is subject to the pseudo second order equation.

Keywords: Activated Carbon, Pomegranate Peels, Adsorption, Thermodynamic, Kinetic.

INTRODUCTION

Water pollution is highly regarded dangerous problems which face the environment and society in the present time, especially after people growth and which is accompanied by the large spread of various industries, more particularly in textiles, approximately all over the world, to avail people needs. So, using dyes in industries has increased, but many of these dyes are poisonous or the results of biological decomposition thus interest removed it from the waste water before it is put into the environment has become vital. The adsorption is considered a more considerable way used in treating water pollution and has the lest costs, particularly when the researchers in this regard enabled to prepare cheap adsorbents in price and from miscellaneous vegetable and industrial residues. The activated carbon has known of the capability of removing the dye materials from aqueous solutions since the 15 century. It had been used in sugar industry to lighten colours. Moreover, it was widely used in gas mask-industry during the first world war and later on, it was more widely used in different fields of the chemical and industrial operations[1].

The activated carbon is known as a porous material has a shortcoming in its crystal structure and deficiency in its hydrogen in the course of its production, this shortcoming leads to the appearance of non-homogenous and unstable pores as for its content of energy or activity, these pores are mostly found in the superficial surfaces of the activated carbon-fines and in other conditions, they are internal. The size of these pores exceeds the size of those found in the inactivated carbon, so their capacity of adsorption is bigger and thus the activated carbon has a high adsorptive capability that exceeds any other material[2].

If we are going to read the literature review in this regard, we will find many ways and materials used in preparing the activated carbon, such as:

Qasim[3]prepared activated carbon by using the date kernels and walnut peels as carbonic raw materials as well as using the asphalten as a connected material; the carbonization process was done through two stages, the first was at 250C^{o} and the second was at 500C^{o} for 1 hour and under the atmosphere of nitrogen gas, then, the activation process was done at 1000C^{o} and by passing a current of nitrogen gas too.

Yamaguchi and Sato[4] enabled to prepare activated carbon by adding some basics like KOH to the thioliguine and later on, treating the product thermally at 600C^{o}. The activated carbon prepared had high adsorptive properties.

Rahman and Saad[5] prepared an activated carbon from *Guava seeds* via thermolysis out of air at 700C^{o} by the existence in chloride zinc as an activated coefficient and the adsorption capacity was measured by the adsorption of methylene blue dye from its aqueous solution.

Al-Ghannam[6] and his group prepared an activated carbon from *Morus nigra* by using increase of potassium hydroxide at 550±25C^{o} for 3 hours.

Aweed[7] enabled to prepare many samples of activated carbon by using some vegetable residues (coco nut peels, date kernels, sun flower peels, and the harvest residues) by means of reacting them with the increase of KOH [1:2] [vegetable residues :basic] at 550± 50C^{o}, for 3 hours.

Al-Baidhany[8] and his group prepared an activated carbon from the kernels of the Iraqi date by using the chemical activation- way, through plunging the kernels in the concentrated solution of phosphoric acid(80%), then, the carbonization process was fulfilled at 400C^{o}.

Ananthabaskaran[9] prepared an activated carbon from the wood apple outer shell and he used the activated carbon prepared to remove the methylene blue dye from its aqueous solution by studying the contact time-effect, the quantity of the adsorbent material, dye concentration, pH and temperature.

Dakheel[10] enabled to prepare an Charcoal from pine wood via reacting it with sodium hydroxide of the ratio [1:1] and [1:2] [wood pine: sodium hydroxide] at 550C^{o}.

Dash[11] made a study of the emulative adsorption for solution composed of three dyes (Congo red, methylene blue, and malachite green) by the trade activated carbon, depending on the capability and efficiency of the activated carbon to adsorption the dyes from their aqueous solutions. The study of the adsorption capacity and the effect of some factors(that are vital in this regard) such as the adsorbent material, temperature, pH, and contact time. This study was achieved in order to treat the liquid-industrial wastes with respect to spinning and textiles and stations of purifying water. These dyes are used in those fields, so there is need to design adsorptive poles used in removing these dyes.

Venckatesh[12] and his companions made an experimental study to adsorption the dye(Direct red-28) by using the activated carbon prepared from punica granatum through the chemical activation with H_2SO_4. The effective factors on the adsorption was studied like: temperature, initial concentration, and pH effect. A kinetic study was made by applying pseudo-first and second order equations and Elovich equation. Furthermore, Langmuir, Freundlich and Tempkin isotherms on the experimental data for the adsorption process. It was found that Langmuir equation was more applicable than the other equations.

Mane[13] and his group enabled to use natural materials like banana and orange peel as adsorbent materials to removal of dyes from waste effluent of textile industry. The adsorption study was made by applying Langmuir and Freundlich isotherms.

Al-Hayali[14] and his group investigated the possibility of using the local bentonite and the activated carbon prepared by the spent lubricating oils through chemical treatment as economic-adsorbent materials to remove copper ions from aqueous solutions by batch way and at different concentrations and temperatures. The study was executed kinetically and thermodynamically by both adsorbent materials. Also, the study included the application of Freundlich and Langmuir isotherms on the experimental data of the adsorption, Langmuir isotherm was more applicable on the studied system practically. The results showed that the used adsorbents in this study were good and could be used (as they are cheap-adsorbent materials) in removing the heavy ions from waters resulted from industrial wastes.

Salman[15] studied preparing the activated carbon from the branches of pomegranate tree(BP) via the physiochemical activation with potassium hydroxide and CO_2 treatment. Also, he studied the effect of temperature activation, activation time, and chemical impregnation ratios on the carbon yield, methylene blue dye(MB) and removing it from its water solution ; the best temperature for activation was at 620C^o, the activation time 1.4 hr, and yield 16% and the ratio of methylene blue dye-removal was 92.5%.

Radaei[16] and his company prepared an activated carbon from the residues of pomegranate and it was activated by H_3PO_4 treatment ,it was used in adsorbing the dye(blue-19), he studied the contact time, pH effect, the adsorption dose and the initial concentration for the dye. The experimental data as for Tempkin isotherm adsorption(R^2=0.975) pseudo second order equation (R^2 = 0.999) and the thermodynamic functions (ΔG^o, ΔH^o and ΔS^o) were calculated.

Moghadam[17] and his group prepared an activated carbon from pomegranate peel via the thermal activation at 500C^o, this kind of carbon was used to adsorb Iron(II) ions from its aqueous solution as well as in studying some variables like: pH, contact time, sorbent weight, metal concentration, and temperature. The adsorption results were applied on the pseudo first and second order equations and the data were applied on Freundlich and Langmuir equation. The calculations showed that the adsorption system was exothermic and it was applicable on Langmuir model and the kinetic model for the pseudo first order. It was found that the prepared material had a high adsorption capability compared with other materials prepared from biotic mass wastes.

EXPERIMENTAL PART

1.1: Preparation of Activated Carbon

Fist: Preparation The Raw Material
It took the raw material (Pomegranate peels) Natural form dry and then milled and transformed into powder.

Second: Preparation of Activated Carbon

A: The Primary Carbonization Process
The raw material prepared in first section was put in a steel container resisting the rust and coated by nickel and was mixed with potassium hydroxide of ratios were about[(1:0.5) - (1:3)] [Pomegranate peels: KOH] and through increase reached 0.5% weight of the basic per reaction. The mixture was homogenized by adding (5-10) ml of distilled water and then heated to a temperature of 350C^o with continuous moving for three hours and until the liberation of the gases stopped.

B: Activation:
The mixture was heated up (550±25)C^o for two hours to complete the activation process. After that, the samples were left to be cold up to the room temperature.

C: Purification of Activated Carbon
The activated carbon prepared was purified by washing it by distilled water many times, then refluxed heat process by using 10% of HCl for 2 hours to remove the biggest number of metals contents as possible. After that, the sample was filtered and washed by distilled water till the washing water became neutral, then, it was dried in the oven at 120C^o for 24 hours and was kept in a closed container.

Third: Preparing samples of an activated carbon from mixtures(pomegranate peels with asphalt), (pomegranate peels with resin Novolak) and (pomegranate peels with asphalt and resin Novolak)
A- Preparing an Activated Carbon from mixture: Pomegranate peels with Asphalt ACPA:

The pomegranate peels were mixed with Beji asphalt, the ratios were about:(5-25%) weight of the asphalt and the increase was 5% wt of the asphalt per sample.

B- Preparing an Activated Carbon from mixture: Pomegranate peels with resin Novolak ACPN:
The pomegranate peels were mixed with the resin novolak which was broken thermally, the ratios were about (5-25%)weight and the increase was 5%wt from the resin novolak per sample.

C- Preparing an Activated Carbon from mixture: Pomegranate peels with Asphalt and resin Novolak, ACPAN:
The pomegranate peels were mixed with the mixture: (asphalt:resin novolak) (1:1), the ratios were about (5-25%) weight and the increase was 5%wt of the mixture per addition.

D- The prepared mixtures in the above items(A, B, and C) were repeated in the steps (A, B, and C) of the second item, by using a constant ratio of potassium hydroxide (1:2.5) (pomegranate peels: KOH), as it was the best ratio used in preparing the activated carbon.

1.2: Conducting some Measuring on Prepared Activated Carbon Samples

1.2.1: Measuring of the Internal Surface Area of Activated Carbon by Adsorption Iodine in its Aqueous Solution

This way is considered one of the familiar and common ways used in calculating the inner superficial area of the activated carbon and it represents the number of iodine milligrams that are under adsorption through the solution by 1gram of the activated carbon. 1gram of the activated carbon was weighed and put in a conic flask has the capacity 250ml and 10ml of 5% HCl; later on, the contents of the flask were heated up to boiling for 30 seconds, then it was cooled up to the laboratory temperature, then, added (100)ml iodine solution, 0.1N. The mixture was shook for half hour, after that, it was filtered and 20ml left at the beginning of the filtering process, 50ml was collected to be standardized with 0.1 N solution of aqueous sodium thiosulfate and by using starch as proof and according to the quantity of sodium thiosulfate used through the burette. Later on, the weight of iodine adsorption from the activated carbon was calculated via applying the following equation[18].

$X=A-[2.2B \times$ ml of Thiosulfate Used] ……..(1)

$A=N_1 \times 12693$ ……..(2)

$B=N_2 \times 126.93$ ……..(3)

X: represents the iodine weight by adsorption mg. via the activated carbon.
N_1: the standardization of iodine solution (0.1 N).
N_2: the standardization of sodium thiosulfate (0.1 N).

Whereas the iodine No. can be calculated by the following equation:

$$In = \frac{X}{M} D.....(4)$$

M: the weight of the activated carbon sample that is used.
D: correction factor.

1.2.2: Measuring the Density

A specific quantity of the activated carbon was put in a voluminous bottle, its capacity 5 ml. which the carbon activated occupying its volume taking into account some minutes in one level at the symbol boundary, then, the carbon found in that voluminous bottle by using a sensitive scales and the density was calculated as follows[19]:

Density(g/cm^3) = mass/volume

1.2.3: Measuring of Ash Content Percentage

1g of the activated carbon was weighed and put in a dish evaporating which was put in an electric oven at 1000 C^o for 3 hours, then it was left to be cooled, after that it was weighed by a sensitive scales to calculate the ash residues for every sample of the activated carbon prepared; later on, the percentage rate of the ash was calculated in every sample[20].

1.2.4: Measuring of Humidity Percentage

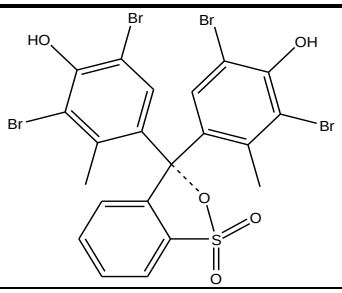
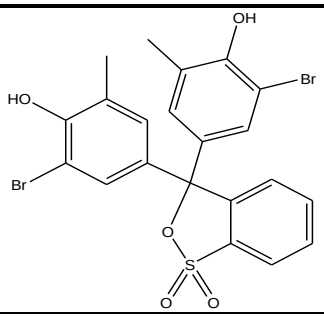
1g of the sample was weighed accurately and put in an oven whose temperature was 150C^{o} for 3 hours, then, it was cooled and weighed accurately and quickly; making differentiations between weights, the humidity content was measured in the form of percentage rate[21].

1.3: Study of Optimum Conditions for Adsorption

This part consisted of studying the favorable conditions for adsorption of the dyes as for the concentrations range used in the material which was under adsorption, the quantity of the adsorption-material, the effect of time contact in reaching the adsorption of the equilibrium condition, and the effect both of the concentration and temperature on the adsorption dyes.

The Used Dyes

Table (1): represents the names of the used dyes and some of their physical characteristics as well as the values λ_{max} of it

Dye name	Structural form	Color	Melting point (C^{o})	λ_{max} (nm)
Bromocresol Green (BCG)		Green yellow	224-226	420
Bromocresol Purple (BCP)		Purple	241-242	428

1.3.1: Preparing the Standard Solutions

A standard solution for all dyes was prepared by the concentrations (10^{-3} M) within a mixture of ethanol-water 50% by solubility a specific weight of dye in a limited quantity of ethanol (50ml), it was diluanted by distilled water up to (100ml). The wavelength was measured of maximum absorption (λ_{max}) for the dyes by means of using the same ratio of ethanol and distilled water as reference solution(Blank).

1.3.2: Effect of Dose on Adsorption Capacity

A specific weights of the activated carbon prepared were taken and they were about (0.01-0.04g) in the volume(20ml), and the concentration was(2×10^{-4}M). It was found that the best quantity used was 0.01g (the dose: 0.5g/L), it is worth mentioning that this quantity of the activated carbon was used in the later study.

1.3.3: Limiting the Equilibrium Time for Adsorption System

Nine solutions having equal volumes and concentrations(2×10^{-4}M) were prepared, also these solutions had the same quantity of the activated carbon prepared and at constant temperature; after the continuous shaking, the nine solutions were filtered and by different times (5, 10, 15, 20, 30, 40, 50, 60, 70) minutes respectively; the adsorption quantities were estimated by means of using the spectrum way.

A calibration curve was executed on each material, at maximum wavelength(λ_{max}) and within the range of concentrations. The adsorption on the special wavelength for each material was followed up. The results showed that getting adsorption time up to the equilibrium condition in all conditions was about(60-70) minutes.

1.3.4: Effect of Concentration

The effect of concentration on the adsorption was investigated according to the following steps:

1- Four solutions having equal volumes were prepared of each dye, by different concentrations, and by the range (1×10^{-4} - 5×10^{-4})M. Also, the same quantity of the activated carbon (0.01g) was added to each solution.
2- The solutions were shaken for (70) minutes by the shaker and then, they were filtered.
3- The percentage rate of adsorption was estimated by using the spectrum way and by the calibration curve for each material. The percentage rate of adsorption was calculated by the following equation:

$$\%ads = \frac{C_{ads}}{C_i} \times 100 \text{.....(5)}$$

C_{ads} : the concentration of the adsorbate-material(mg/L)

C_i : The initial concentration(mg/L)

1.3.5: Effect of Temperature

The effect of temperature was studied on the adsorption by applying the following steps:

1- After specifying the concentration which has triggered at higher adsorption rate, it was selected to prepare five solutions consisting of the same concentrations of the solutions dyes and the same quantity of the activated carbon.
2- The solutions were shaken separately for(70) minutes and at temperatures (15, 25, 35, 45, 55)C^o respectively, by using the shaker which has water bath inside(programmed) that its temperature was run exactly.
3- The solutions were filtered, The absorption values were recorded , and the capacity of spectrum adsorption was estimated by using the following equation:

$$q_e = \frac{C_i - C_e}{m} \times V \text{.....(6)}$$

q_e : represents the adsorption capacity at the equilibrium (mg/L)

C_i : represents the initial concentration of the dye(mg/L)

C_e : represents the concentration of the dye's rest in the solution at the equilibrium

m: the weight of the adsorbent material(activated carbon) (gm)
V: the volume solution used in estimating the adsorption(L)

1.3.6: Calculating the Thermodynamic Functions

The values of the equilibrium constant for adsorption (K) at different temperatures in the equilibrium condition were calculated as for the ratio between the adsorbate concentration and the residues of the concentration for the dye solution, whereas the values of the thermodynamic functions of the equilibrium (ΔG^o, ΔH, ΔS^o) were calculated by using equations. The adsorption enthalpy can be calculated by applying Vant Hoff equation which represents the relation between the equilibrium constant and temperature.

$$K = K_0 e^{-\Delta H/\ RT} \text{.....(7)}$$

Where (ΔH) represents the adsorption temperature (adsorption enthalpy), (K) is the adsorption-equilibrium constant, whereas (K_o) represents a constant value. By taking the ln for both sides, we can get on the following form of the equation:

$$\ln K = \ln K_0 - \frac{\Delta H}{RT} \text{.....(8)}$$

The value (ΔH) can be calculated by drawing the relation between ($\ln K$) in opposite to the reversed temperature (l/T) which gives a straight line whose slop is equal to - $\Delta H/R$. The other thermodynamic functions (ΔG^o, ΔS^o)can be calculated by the following equations:

$$\Delta G^0 = -RT\ \ln K \text{.....(9)}$$

$$\Delta G^0 = \Delta H - T\Delta S^0 .....(10)$$

$$\Delta S^0 = (\Delta H - \Delta G^0)/T .....(11)$$

1.3.7: Applying Freundlich, Langmuir & Tempkin Isotherms on the Adsorption of Dyes with the Activated Carbon

The values of Freundlich constants(K_f , n) were calculated from drawing the relation between the value $\log q_e$, $\log C_e$ according to the following equation:

$$\log q_e = \log K_f + 1/n \log C_e .....(12)$$

q_e represents the adsorption capacity at the equilibrium(mg/g), C_e is the concentration of the dye remainder in the solution during the equilibrium (mg/L), K_f , n are Freundlich constants, The value of n has a relation to the adsorption intensity and its value indicating to the favorable adsorption when it becomes within the range (1-10), but it refers to the chemical adsorption when its value is less than 1. Whereas the value of K_f has a relation to the adsorption capacity[22].

By the same way, Langmuir constants(b) were calculated as well as the maximum capacity of adsorption from drawing the relation between C_e/q_e in opposite to C_e and according to the following equation[23]:

$$\frac{C_e}{q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}} .....(13)$$

Q_{max} represents the value of maximum theoretical adsorption capacity for the adsorbent(mg/L), whereas b represent a constant having a relation to the correlation strength of the dye through the adsorption surface.
Similarly, Tempkin constants (K_T, B_T) were calculated from drawing the relation between the value q_e in opposite to $\ln C_e$ according to the following equation:

$$q_e = B_T \ln K_T + B_T \ln C_e .....(14)$$

B_T is referring to a constant having a relation to the differential capacity surface as to adsorption capacity for each power unit of link, whereas K_T (L/mg) represents a linkage constant of equilibrium and it indicates to the maximum linkage energy[24].

1.3.8: Kinetic Study Adsorption
1.3.8.1: The Application of Pseudo First Order Equation and the Pseudo Second Order Equation

Pseudo first order equation[25,26]

$$\ln(q_e - q_t) = \ln q_e - k_1 t .....(15)$$

Pseudo-second order equation[27,28]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t .....(16)$$

1.3.8.2: The Application of Elovich Equation and the Equation of Intra Particle Diffusion

The sample of the kinetic Elovich equation was experimented on the process data for dyes adsorption on the activated carbon prepared and under the conditions mentioned previously through drawing the relation between the adsorption capacity at specific times(q_t) in opposite to $\ln t$ and in terms of the following equation[29]:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t .....(17)$$

α represents the rate of the initially adsorption speed (mg. $g^{-1}.min^{-1}$) and β represents the adsorption constant ($g.mg^{-1}$) through any one test. Similarly, the equation of intra particle diffusion was applied on the process data, by drawing the relation between the adsorption capacity at different times (q_t mg/g) in opposite to ($t^{1/2}$), and from the linear relation that was got is possible to calculate C(mg. g^{-1}) of the straight line section which has a relation to the layer thickness- limit of the liquid which is next to the solid surface (mg/g), has K_{diff} ($mg.g^{-1}.min^{-1/2}$) in, which represents the velocity of the intra particle diffusion and according to the following equation[30].

$$q_t = K_{diff}\ t^{1/2} + C .....(18)$$

RESULTS AND DISCUSSION

The production of the activated carbon, as it has been written in the literature review, depends essentially on using raw materials having a high carbon content with carbonizing stuffs like the concentrated and smoky H_2SO_4, free sulfur, or HCl with using different activation conditions that might be hot or vaporific. As far as this research is concerned, an activated carbon was prepared from vegetable source, definitely the pomegranate peels as it is shown in first item of the practical part, Table(2) shows the results that have been got.

Table(2): The properties of the activated carbon prepared from pomegranate peels

samples	Raw material : KOH	Iodine number (mg/g)	Density (g/cm^3)	Ash content %	Humidity content %	Yield %
C_n	1:0	339.420	0.397	3.21	9.07	21.705
1	1:0.5	654.959	0.383	3.19	8.13	20.401
2	1:1	674.507	0.306	3.17	10.55	18.810
3	1:1.5	710.808	0.292	3.14	10.76	16.528
4	1:2	780.620	0.273	3.08	10.88	14.904
5	1:2.5	822.507	0.261	3.02	11.87	13.327
6	1:3	788.997	0.281	4.00	7.03	8.800
B.D.H.*	-	908	0.345	3.200	0.80	-

* reference [31]

C_n: Activated Carbon Prepared from pomegranate peels without any material addition.

We can notice from the table above that the increase of the added basic leads to the increase in the iodine adsorption values from its solution up to the ratio (1: 2.5), we can notice that these values begin at decreasing. This is due to the hydroxide increase results in breaking part of the forming gaps and pores on the surface of activated carbon prepared at the rate(1: 3).

The existence of hydroxyl ion in the potassium hydroxide leads to decay in the raw material structure and thus, it leads to developing the porous structure for the carbon produced[32].

Also, we can notice, in the table, that the ash content is within the allowable limits due to using the refluxed heat process with HCl, which works on removing the biggest part of the metallic components in addition to removing any trace of the basic[33].

As for the values of humidity content, they were about (7.03-11.87)% it is a relative measure showing the degree of the capability of using the prepared samples in the adsorption process of vapor water. It was shown that some samples could be used as adsorbents for vapor water.

The density- values were about (0.281-0.383)gm/cm^3, they were low values as the nature of raw material having high porosity, and then, the material produced would have low density and high porosity, this was demonstrated by the adsorption values which had a reflexive relation to the density.

As for the yield, we can notice that the values decrease when the potassium hydroxide added increases, this is normal as increasing the ratio of the basic added leads to increase in the loss- rate within the carbon content of the raw material, and thus, decreasing in the yield.

The activated carbon prepared was chosen of the ratio (1: 2.5), sample(5) to be used in adsorbing the dyes under study, because it gave higher iodine no. 822.507 mg/g. It was used in studying the adsorption of the two dyes mentioned in the table (1) so as to testing the adsorption efficiency of the carbon prepared. In an attempt to improve the properties of the activated carbon prepared from pomegranate peels, the raw material was treated with some added substances represented by the asphalt, resin novolak, and mixture of the asphalt and resin novolak; the process

of preparing the activated carbon has been done as it is shown in the item (1.1) of the practical part and the tables (3,4,5) explain the results that have been got:

Table (3): The properties of the activated carbon prepared from mixture (Pomegranate peels with Beji Asphalt) by using (1:2.5) (raw material:KOH)

Samples	Beji Asphalt %	Iodine number (mg/g)	Density (g/cm^3)	Ash content %	Humidity content %	Yield %
7	5	830.884	0.256	3.01	11.89	14.105
8	10	864.394	0.218	2.94	11.42	15.232
9	15	881.149	0.178	2.82	12.01	16.034
10	20	900.696	0.118	1.75	12.20	17.691
11	25	925.828	0.080	1.68	12.38	21.631
B.D.H.*	-	908	0.345	3.200	0.80	-

Table(4): The properties of the activated carbon prepared from mixture (Pomegranate peels with resin Novolak) by using (1:2.5) (raw material:KOH)

Samples	resin Novolak %	Iodine number (mg/g)	Density (g/cm^3)	Ash content %	Humidity content %	Yield %
12	5	836.469	0.221	2.98	11.93	14.831
13	10	892.318	0.210	2.92	11.47	16.243
14	15	945.375	0.196	2.54	12.41	18.284
15	20	976.092	0.106	1.87	12.29	20.072
16	25	1004.017	0.075	1.23	13.71	22.471
B.D.H.*	-	908	0.345	3.200	0.80	-

Table(5): The properties of the activated carbon prepared from mixture (Pomegranate peels with the Asphalt and the resin Novolak) by using (1:2.5) (raw material:KOH)

Samples	Mixed(Asphalt, resin Novolak) %	Iodine number (mg/g)	Density (g/cm^3)	Ash content %	Humidity content %	Yield %
17	5	864.394	0.220	2.86	11.98	14.907
18	10	981.677	0.186	2.75	11.59	18.071
19	15	995.639	0.144	2.08	12.61	19.231
20	20	1017.979	0.104	1.72	12.74	27.580
21	25	1129.677	0.064	1.79	13.92	34.410
B.D.H.*	-	908	0.345	3.200	0.80	-

The aim of using the added substances is to improve the adsorptive features for the samples of activated carbon prepared. These added things were chosen because they contain aromatic structures, so this gives the activated carbon prepared a form resembles the graphite in its structure and consequently, this leads to improving the adsorptive properties for the carbon produced.

We notice of the tables that using the added materials have improved of the activated carbon capability for adsorption, the maximum value was in using a constant mixture of the asphalt and resin novolak (1:1), and the ratios were about (5-25%)wt of the mixture.

The process of using mixtures gave us samples having high efficiency of adsorption higher than that found in the trade activated carbon which was produced by B.D.H. company.

Also, we can notice of the tables that the yield of the activated carbon increases in the course of the increasing of the added ratio of pomegranate peels, this is may be due to the increasing of the added rate to the pomegranate peels leads to happening of reactions which increase the carbonic mass; this reflects on the yield that the produced carbon yield increases during increasing the carbonic mass of the raw material. The maximum rate of yield has been got by using mixture of asphalt + resin novolak 25%; it reached 34.410% which was very excellent ratio in feasibility of the economic process. What was said about ash content, humidity and density in the table(2) was completely applicable on the got values by using the mixtures.

Table(6): Samples of the activated carbon prepared chosen for the study depending on giving them the highest iodine number

Samples	Type Activated Carbon Prepared	Code briefly	Iodine number mg/g	pH V:V Ethanol : Distillation Water %50
5	Activated Carbon Prepared from [Pomgranate Peel:KOH] by ratio(1:2.5)	ACP	822.507	5.23
11	Activated Carbon Prepared from mixed [Pomgranate Peel: 25% Beji Asphalt] by using (1:2.5)(raw material:KOH)	ACPA	925.828	8.00
16	Activated Carbon Prepared from mixed [Pomgranate Peel: 25% Novolak resin] by using (1:2.5)(raw material:KOH)	ACPN	1004.017	8.63
21	Activated Carbon Prepared from mixed [Pomgranate Peel: 25% Beji Asphalt with Novolak resin] by using (1:2.5)(raw material:KOH)	ACPAN	1129.677	8.72

To follow up this study at spectrum way, it is necessary to find the values(λ_{max}) for these dyes, then making a calibration curve for each dye and within the range of concentration which is compatible to the colour intensity of these dyes. The calibration curves were achieved by depending on Lambert Beer's law which can be expressed by the following equation:

$$A = \varepsilon LC \text{.....} (19)$$

A: represents the absorption of the dye, ε : the factor of the absorption molar (Liter.mol^{-1}.cm^{-1}), *L*: the length of the light line for the visible rays (L=1 cm), and *C*: the molar concentration (mol.Liter^{-1}). The selected dyes in this study showed that they were suitable to Lambert Beer's law represented by linear relations which were got by drawing the absorbance relation (A) in front of the concentration.

1:Effect of adsorbent dose

Studying the Effect of the adsorbent on Adsorption the dyes (BCG, BCP) and at different initial concentrations at 139.602 and 108.048 mg/L respectively, with changing the adsorbent dose within the range 0.5-2.0 g/L. These experiments were achieved at 25C^{o} and the results which were got, were listed in the following table:

Table(7): The effect of the activated carbon quantity on the adsorption capacity at 25C° and an initial concentration (2×10^{-4} M)

Type Activated carbon prepared	Dye	Dose (gm/L)	C_i mg/L	C_e mg/L	q_e mg/g	%ads.
ACP	BCG	0.5	139.602	18.846	241.512	86.50
		1.0		18.148	121.454	87.00
		1.5		11.866	85.157	91.50
		2.0		6.282	66.66	95.50
	BCP	0.5	108.048	39.437	137.222	63.50
		1.0		32.414	75.634	70.00
		1.5		21.609	57.626	80.00
		2.0		16.207	45.920	85.00
ACPA	BCG	0.5	139.602	16.752	245.7	88.00
		1.0		16.054	123.548	88.50
		1.5		12.564	84.692	91.00
		2.0		9.074	65.264	93.50
	BCP	0.5	108.048	18.368	179.36	83.00
		1.0		17.287	90.761	84.00
		1.5		16.747	60.867	84.50
		2		12.965	47.541	88.00
ACPN	BCG	0.5	139.602	13.960	251.284	90.00
		1.0		12.564	127.038	91.00
		1.5		11.866	85.157	91.50
		2.0		10.470	64.566	92.50
	BCP	0.5	108.048	3.781	208.534	96.50
		1.0		3.241	104.807	97.00
		1.5		2.701	70.231	97.50
		2.0		2.701	52.673	97.50
ACPAN	BCG	0.5	139.602	13.262	252.68	90.50
		1.0		12.564	127.038	91.00
		1.5		11.168	85.622	92.00
		2.0		6.980	66.311	95.00
	BCP	0.5	108.048	2.701	210.694	97.50
		1.0		2.701	105.347	97.50
		1.5		2.701	70.231	97.50
		2.0		1.620	53.214	98.50

Noticing the table above, we find that there is decrease in adsorption- capacity in the course of increasing the dose of adsorbent material quantity used and this differentiation can be explained in the relation of adsorption capacity in addition to its efficiency with adsorbent material quantity change as follows:

Obviously, the number of spots that are qualified to adsorption increases when the adsorbent- material quantity increases. This increase improves the adsorbent material efficiency to remove the dye from its aqueous solution. But that causes decrease in the adsorption capacity during calculating it mathematically with reference to the adsorbate material per mass unity of the adsorbent material (mg/g), where the increase in the adsorbent material quantity will leave effective sites for adsorption that are empty in while using a constant concentration of adsorbate.

The results got are compatible with other results seen in similar studies in the literature, where they were explained by two perspectives; first: the decrease in adsorption capacity with the increase of adsorbent quantity was due to the slowness and non-saturation of the efficient spots for adsorption in the course of the adsorption- process[34,35].

The second perspective represents other view point, the researchers argued that the reason behind this change might form intra-particle intersections between the adsorbent molecules. The increase in the adsorbent quantity results in conglomerating it because of these intersections. Accordingly, the whole superficial area for the adsorbent decreases and this leads to increase in the length of molecules diffusion- tracks that are adsorbate through[36].

2: Effect of contact time

The contact time is regarded one of the most important variables which can be used to assess the information as for the experimental application for the adsorption process, particularly in the kinetic study. This study was achieved by fixing all the variables which react on the adsorption process except the time. The time effect was calculated at an initial concentration 2×10^{-4}M for the two dyes, and by shaking a specific volume of dye solution (20 ml) and by using a constant quantity of the activated carbon (0.01g) at temperature 25C^{o}. The results got were listed in the following table:

Table(8): The effect of contact time on the capacity adsorption at 25C^{o}, initial concentration 2×10^{-4}M, the speed of shaking: 100 circle/min and the volume of dye solution: 20ml

Type Activated carbon prepared	Dye	Time (min)	C_i mg/L	C_t mg/L	q_t mg/g	%ads.
ACP	BCG	5	139.602	69.801	139.602	50
		10		50.256	178.692	64.00
		15		48.860	181.484	65.00
		20		40.484	198.236	71.00
		30		27.920	223.364	80.00
		40		25.128	228.948	82.00
		50		22.336	234.532	84.00
		60		18.846	241.512	86.50
		70		18.148	242.908	87.00
	BCP	5	108.048	102.645	10.806	5.00
		10		75.633	64.83	30.00
		15		64.828	86.44	40.00
		20		59.426	97.244	45.00
		30		52.403	111.29	51.00
		40		43.219	129.658	60.00
		50		42.138	131.658	61.00
		60		39.437	137.222	63.50
		70		37.816	140.464	65.00
		5		28.618	221.968	79.50

ACPA	BCG	10	139.602	23.034	233.136	83.50
		15		22.336	234.532	84.00
		20		21.638	235.928	84.50
		30		20.242	238.72	85.50
		40		18.846	241.512	86.50
		50		17.450	244.304	87.50
		60		16.752	245.7	88.00
		70		16.752	245.7	88.00
	BCP	5	108.048	41.598	132.9	61.50
		10		21.609	172.878	80.00
		15		21.069	173.958	80.50
		20		20.529	175.038	81.00
		30		19.988	176.12	81.50
		40		19.448	177.2	82.00
		50		18.908	178.28	82.50
		60		18.368	179.36	83.00
		70		17.287	181.522	84.00
ACPN	BCG	5	139.602	34.900	209.404	75.00
		10		33.504	212.196	76.00
		15		27.222	224.76	80.50
		20		25.826	227.552	81.50
		30		24.430	230.344	82.50
		40		23.732	231.74	83.00
		50		14.658	249.888	89.50
		60		13.960	251.284	90.00
		70		13.960	251.284	90.00
	BCP	5	108.048	11.885	192.326	89.00
		10		10.264	195.568	90.50
		15		8.643	198.81	92.00
		20		8.643	198.81	92.00
		30		8.103	199.89	92.50
		40		5.402	205.292	95.00
		50		4.321	207.454	96.00
		60		3.781	208.534	96.50
		70		3.781	208.534	96.50
	BCG	5	139.602	54.444	170.316	61.00
		10		50.256	178.692	64.00
		15		47.464	184.276	66.00
		20		34.900	209.404	75.00

ACPAN		30		22.336	234.532	84.00
		40		14.658	249.888	89.50
		50		13.960	251.284	90.00
		60		13.262	252.68	90.50
		70		13.262	252.68	90.50
	BCP	5	108.048	9.184	197.728	91.50
		10		9.184	197.728	91.50
		15		4.862	206.372	95.50
		20		4.862	206.372	95.50
		30		4.321	207.454	96.00
		40		4.321	207.454	96.00
		50		3.781	208.534	96.50
		60		2.701	210.694	97.50
		70		2.160	211.776	98.00

Noticing the results listed in the table(8), we find that the efficiency of the activated carbon prepared adsorbing the dye BCG was bigger than its efficiency to adsorb the dye BCP, the adsorption- efficiency exceeded 60% in the first dye in the first ten minutes, whereas the adsorption- efficiency for the second dye was 30%. Later on, we find that adsorption- efficiency increases gradually in orderly form and reaches the equilibrium state at contact time : 70 minute in both dyes; this time was used to complete the next study.

3: Effect of initial concentration

The initial concentration is regarded as an important factor in studying the mass transform in the solutions and forming one of the significant powers which is controlling the adsorption process and necessary to overcoming the resistance appeared by molecules for movement from aqueous solution that is transform between two phases: liquid and solid. So, it was seen that there was no study without tackling the effect of concentration in order to determining the optimal conditions for adsorption system. In this research, the effect of concentration of the dyes under studying was studied at the range (1×10^{-4} - 5×10^{-4}) M at the temperature $15C^{o}$, the solution(20ml) of each dye was shaken in constant speed 100 cycle/min and by using the same quantity of the adsorbent material 0.01g for 70 minutes. The results which have been got from this study listed in the following table:

Table (9): The concentration effect on the adsorption capacity at $15C^{o}$, the time of shaking: 70 min, the activated carbon weight: 0.01g, the velocity of shaking: 100 cycle/min and the solution volume of the dye:20ml

Type Activated carbon prepared	Dye	C_i mg/L	C_e mg/L	C_{ads}	q_e mg/g	%ads.
ACP	BCG	69.801	6.282	63.519	127.038	91.00
		139.602	17.450	122.152	244.304	87.50
		209.403	39.786	169.617	339.234	81.00
		279.204	53.746	225.458	450.916	80.75
		349.005	90.741	258.264	516.528	74.00
	BCP	54.024	12.425	41.599	83.198	77.00
		108.048	37.276	70.772	141.544	65.50
		162.072	64.828	97.244	194.488	60.00
		216.096	91.840	124.256	248.512	57.50
		270.12	118.852	151.268	302.536	56.00

ACPA	BCG	69.801	4.886	64.915	129.83	93.00
		139.602	15.356	124.246	248.492	89.00
		209.403	45.370	164.033	328.066	78.33
		279.204	62.820	216.384	432.768	77.50
		349.005	83.761	265.244	530.488	76.00
	BCP	54.024	5.942	48.082	96.164	89.00
		108.048	12.425	95.623	191.246	88.50
		162.072	30.793	131.279	262.558	81.00
		216.096	43.219	172.877	345.754	80.00
		270.12	64.828	205.292	410.584	76.00
ACPN	BCG	69.801	5.584	64.217	128.434	92.00
		139.602	13.960	125.642	251.284	90.00
		209.403	24.430	184.973	369.946	88.33
		279.204	32.806	246.398	492.796	88.25
		349.005	53.048	295.957	591.914	84.80
	BCP	54.024	1.080	52.944	105.888	98.00
		108.048	3.781	104.267	208.534	96.50
		162.072	5.402	156.67	313.34	96.00
		216.096	8.643	207.453	414.906	96.00
		270.12	16.207	253.913	507.913	94.00
ACPAN	BCG	69.801	5.584	64.217	128.434	92.00
		139.602	12.564	127.038	254.076	91.00
		209.403	34.900	174.503	349.006	83.33
		279.204	58.632	220.572	441.144	79.00
		349.005	90.741	258.264	516.528	74.00
	BCP	54.024	1.080	52.944	105.888	98.00
		108.048	2.160	105.888	211.776	98.00
		162.072	4.862	157.21	314.42	97.00
		216.096	8.643	207.453	414.906	96.00
		270.12	14.586	255.534	511.068	94.60

The results above showed that adsorption capacity increased when there was increase in concentration, but adsorption efficiency (percentage of Adsorption) decreased when the concentration increased; this was due to the increasing in concentration at the beginning of adsorption, increased the number of molecules available for adsorption when the sites are eligible for the adsorption on the solid surface available and with the passage of time increased the competition between dye molecules to be connected on the effected remaining-spots, on the surface of constant quantity of the activated carbon used in concentration increase. Furthermore, the concentration increase resulted in remaining larger quantity of dye within the solution after the equilibrium process and this reduced of adsorption -efficiency in the course of calculating it mathematically as to the ratio between the adsorbate to the remainder quantity- material in the solution.

4: Effect of temperature

The study of temperatures influencing on the adsorption process is considered of the very significant studies, this can give the researchers much of information related to the studied system; it makes the calculation and assessment of the thermodynamic functions(ΔG^o, ΔH and ΔS^o) easier, they explain the kind of powers which connects the adsorbent surface with polluted material and assessing the kind and nature of the adsorption process; as well as; the possibility of giving the researcher information which illustrating the direction of the process happening, the system needs or not to have external conditions for executing the process and arranging the system and nature of the powers running the adsorption operation, whether it is physical or chemical.

For these reasons, the effect of temperatures on the mentioned dyes at an initial concentration 2×10^{-4}M, in the range of temperatures 15-55C^o, by using a constant volume of dye solution (20ml) and a constant quality of the adsorbent material 0.01g. The solutions were shaken for 70 minutes and in fixed velocity was 100 cycle/min. The results got are shown in the following table:

Table(10): The effect of temperatures on the adsorption capacity at 15-55C^o, time shaking: 70 min, the carbon activated weight: 0.01g, the speed of shaking: 100cycle/min and the volume of dye solution: 20ml

Type Activated carbon prepared	Dye	Temp. C^o	C_i mg/L	C_e mg/L	C_{ads}	q_e mg/g	%ads.
ACP	BCG	15	139.602	17.450	122.152	244.304	87.50
		25		18.148	121.454	242.908	87.00
		35		20.940	118.662	237.324	85.00
		45		30.014	109.588	219.176	78.50
		55		32.108	107.494	214.988	77.00
	BCP	15	108.048	37.276	70.772	141.544	65.50
		25		37.816	70.232	140.464	65.00
		35		44.839	63.209	126.418	58.50
		45		50.242	57.806	115.612	53.50
		55		52.403	55.645	111.29	51.50
ACPA	BCG	15	139.602	15.356	124.246	248.492	89.00
		25		16.752	122.85	245.7	88.00
		35		20.242	119.36	238.72	85.50
		45		21.638	117.964	235.928	84.50
		55		25.826	113.776	227.552	81.50
	BCP	15	108.048	12.425	95.623	191.246	88.50
		25		17.287	90.761	181.522	84.00
		35		28.092	79.956	159.912	74.00
		45		34.035	74.013	148.026	68.50
		55		41.058	66.99	133.98	62.00
		15		13.960	125.642	251.284	90.00

ACPN	BCG	25	139.602	13.960	125.642	251.284	90.00
		35		29.316	110.286	220.572	79.00
		45		51.652	87.95	175.9	63.00
		55		54.444	85.158	170.316	61.00
	BCP	15	108.048	3.781	104.267	208.534	96.50
		25		3.781	104.267	208.534	96.50
		35		5.942	102.106	204.212	94.50
		45		9.724	98.324	196.648	91.00
		55		10.264	97.784	195.568	90.50
ACPAN	BCG	15	139.602	12.564	127.038	254.076	92.00
		25		13.262	126.34	252.68	90.50
		35		16.054	123.548	247.096	88.50
		45		30.712	108.89	217.78	78.00
		55		36.296	103.306	206.612	74.00
	BCP	15	108.048	2.160	105.888	211.776	98.00
		25		2.160	105.888	211.776	98.00
		35		6.482	101.566	203.132	94.00
		45		7.563	100.485	200.97	93.00
		55		10.804	97.244	194.488	90.00

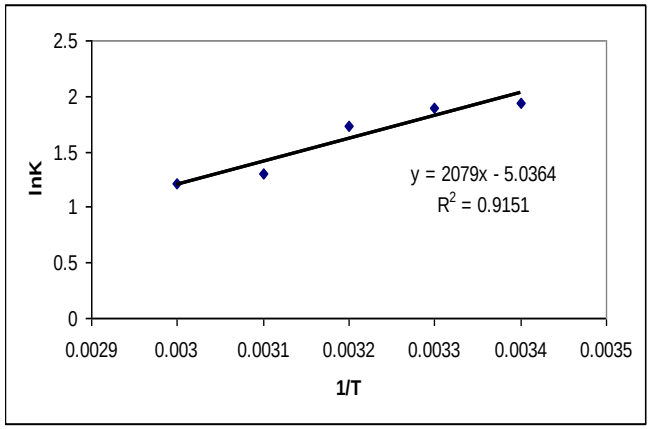
The results listed in the table(10) that adsorption- capacity and efficiency are becoming better at low temperatures and thus, this is having an important field in the economic side in the course of designing adsorption systems as well as it can give denotation that the nature of the powers running the adsorption process in the studied system has a physical nature.

5: Calculation of thermodynamic functions

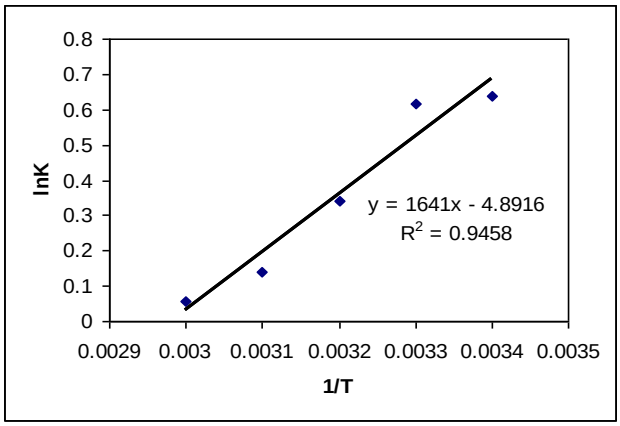
The thermodynamic functions are regarded important variables which give a considerable explanation during the study of adsorption process. They describe the nature of the investigated system, the kind of powers that controlling and driving the adsorption process, as well as they can give an idea about the sort of molecule intersections which might happen through the adsorption process and which might have an important role in determining its efficiency.

The thermodynamic functions were calculated so as to reach these influences and having information explains the system nature (dye-activated carbon) by depending on the change happening during the study of temperature effect and with fixing all other conditions which influence on the adsorption efficiency.

The values of the thermodynamic functions were calculated according to the mentioned equations in the item(1.3.6) and all the graphic drawings in this research were achieved by using the program(Excel). The calculated results in this study (K, ΔG^o, ΔH, and ΔS^o) were listed in the table(11), whereas the figures(1,2,3,4) detect the linear relations formed by drawing lnK in opposite to 1/T in the course of the application of Vant Hoff equation (8) used in calculating the values of change in the enthalpy.

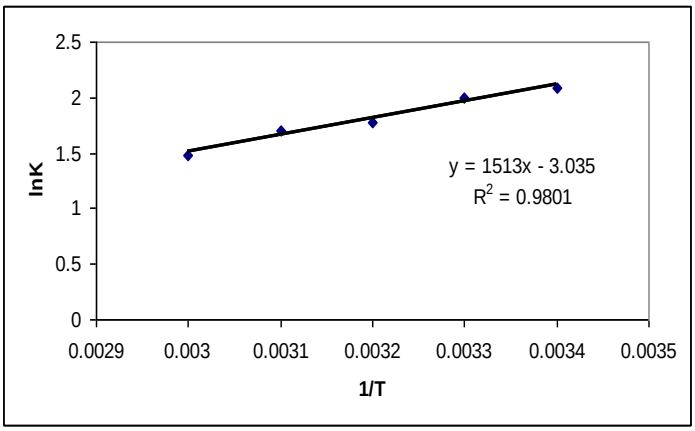


(a) BCG

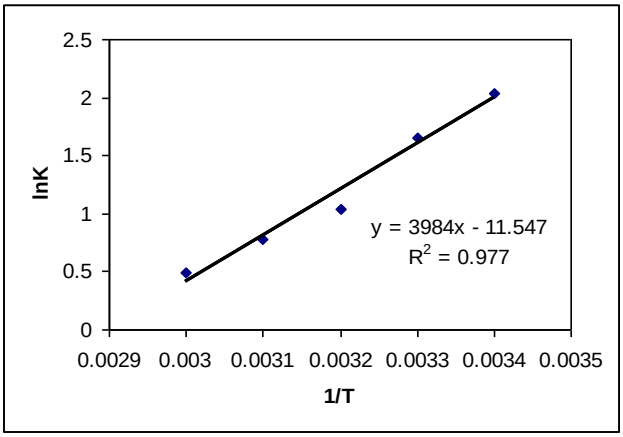


(b) BCP

Figure (1): The relation between lnK in opposite to 1/T to calculate the value of Adsorption enthalpy for two dyes by using the activated carbon prepared ACP

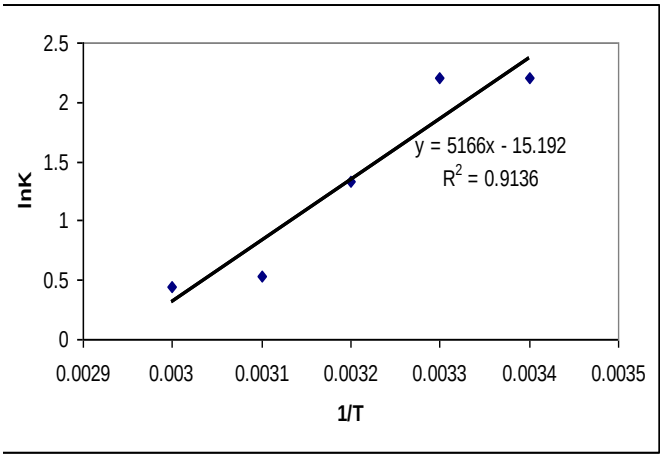


(a) BCG

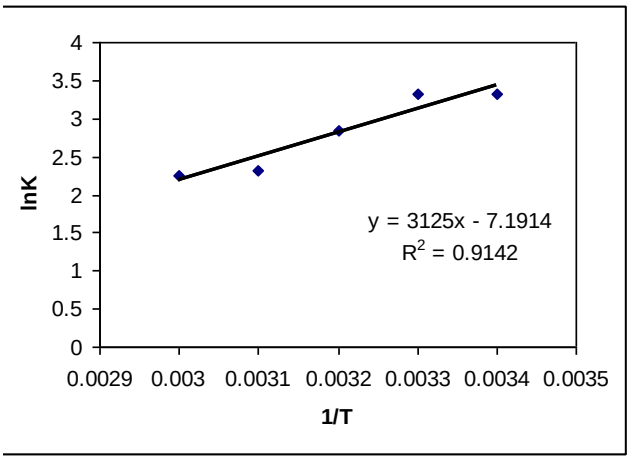


(b) BCP

Figure (2): The relation between lnK in opposite to 1/T to calculate the value of Adsorption enthalpy for two dyes by using the activated carbon prepared ACPA

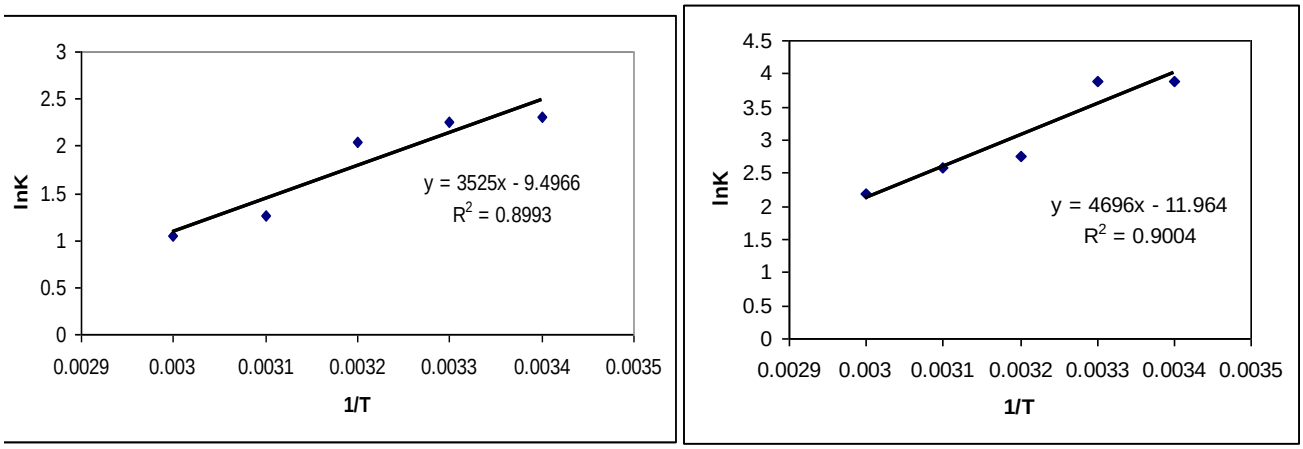


(a) BCG



(b) BCP

Figure (3): The relation between lnK in opposite to 1/T to calculate the value of Adsorption enthalpy for two dyes by using the activated carbon prepared ACPN



(a)BCG **(b)BCP**

Figure (4): The relation between lnK in opposite to 1/T to calculate the value of Adsorption enthalpy for two dyes by using the activated carbon prepared ACPAN

Table(11): The values of the equilibrium constants and the thermodynamic functions during the equilibrium of adsorption for two dyes

Type Activated carbon prepared	Dye	Temp K°	K	ΔH (KJ.mol⁻¹)	ΔG° (KJ.mol⁻¹)	ΔS° (J.mol ⁻¹.K⁻¹)
ACP	BCG	288	7	-17.284	-4.657	-43.845
		298	6.692		-4.707	-42.206
		308	5.666		-4.440	-41.703
		318	3.651		-3.423	-43.588
		328	3.347		-3.294	-42.654
	BCP	288	1.898	-13.643	-1.532	-42.051
		298	1.857		-1.531	-40.644
		308	1.409		-0.875	-41.452
		318	1.150		-0.367	-41.747
		328	1.061		-0.160	-41.104
ACPA	BCG	288	8.091	-12.579	-5.004	-26.301
		298	7.333		-4.935	-25.650
		308	5.896		-4.542	-26.092
		318	5.451		-4.481	-25.464
		328	4.405		-4.041	-26.029
	BCP	288	7.696	-33.122	-4.884	-98.049
		298	5.250		-4.107	-97.366
		308	2.846		-2.675	-98.854
		318	2.174		-2.051	-97.708
		328	1.631		-1.333	-96.919
		288	9		-5.260	-130.866
		298	9		-5.443	-125.861

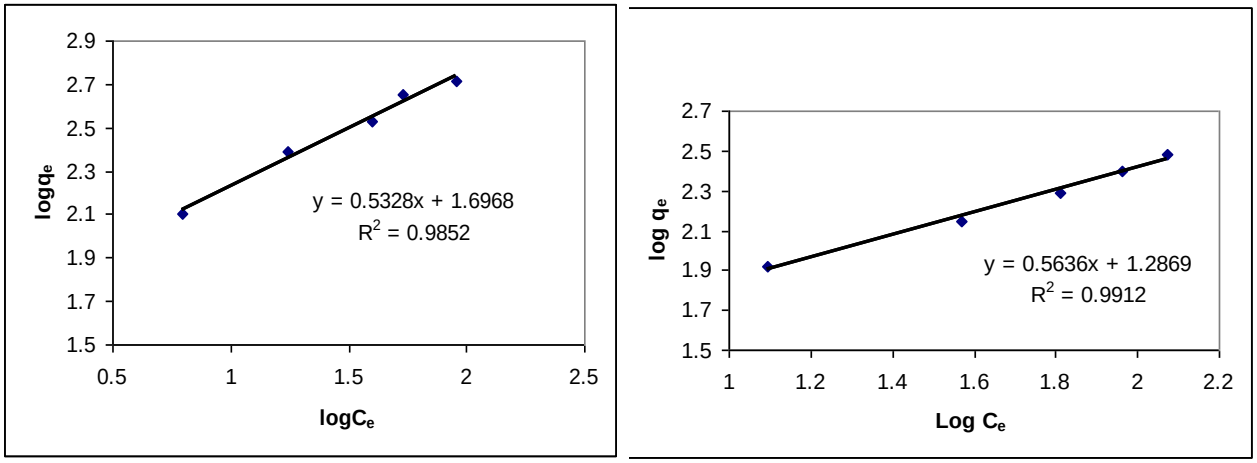
ACPN	BCG	308	3.761	-42.950	-3.390	-128.440
		318	1.702		-1.403	-130.648
		328	1.564		-1.218	-127.229
	BCP	288	27.576	-25.981	-7.939	-62.643
		298	27.576		-8.215	-59.616
		308	17.183		-7.280	-60.718
		318	10.111		-6.115	-62.471
		328	9.526		-6.149	-60.463
ACPAN	BCG	288	10.111	-29.306	-5.538	-82.529
		298	9.526		-5.584	-79.605
		308	7.695		-5.223	-78.191
		318	3.545		-3.344	-81.642
		328	2.846		-2.849	-80.662
	BCP	288	49.022	-39.042	-9.319	-103.206
		298	49.022		-9.642	-98.657
		308	15.668		-7.044	-103.889
		318	13.286		-6.837	-101.275
		328	9		-5.991	-100.766

The results of thermodynamic study listed in the table(11) indicate that the adsorption system under study is an exothermic process, it is controlled by physical powers, (Vander vals' forces) ones which represent connected bonds between the dye and adsorptive surface as well as the adsorption- process in this system occurs spontaneously towards the linking formula with the surface, leading to reducing the system randomness.

6: Adsorption isotherm

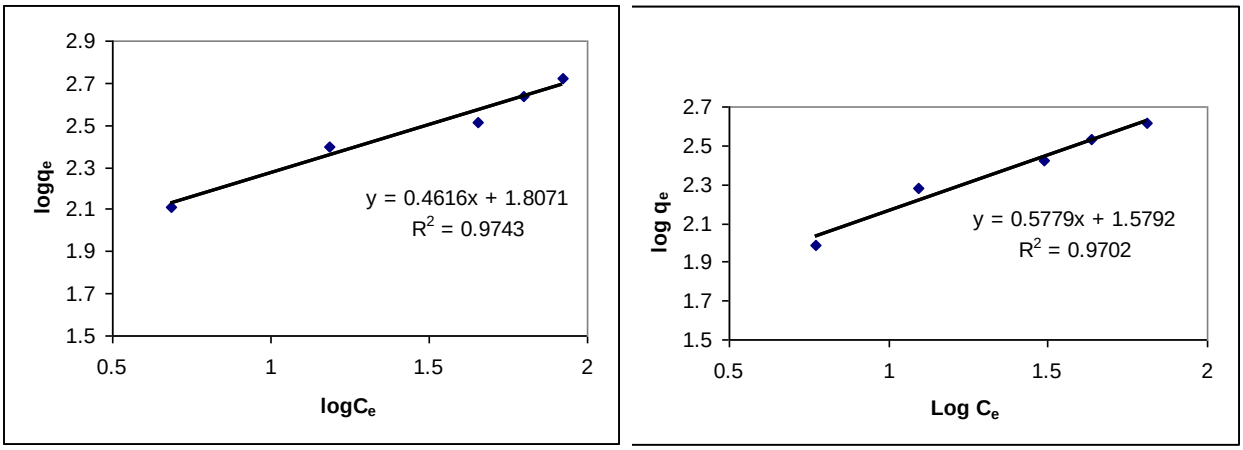
6.1: Freundlich isotherm

Freundlich isotherm (equation 12) was applied on the experimental data for the two dyes and the values of Freundlich constants (K_f , n) from the slop and section of the straight line formed from drawing the relation between $Logq_e$ in opposite to $LogC_e$ respectively. The results which were got, were listed in the table (12) and were graphically shown in the figures(5,6,7,8).



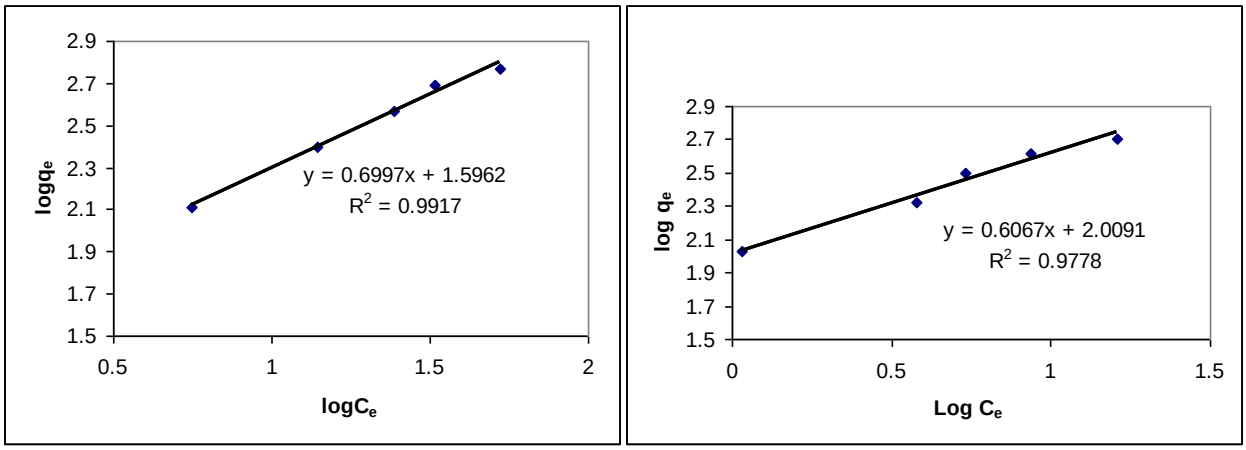
(a) BCG **(b) BCP**

Figure (5): Freundlich isotherm for two dyes adsorption by using the activated carbon prepared ACP



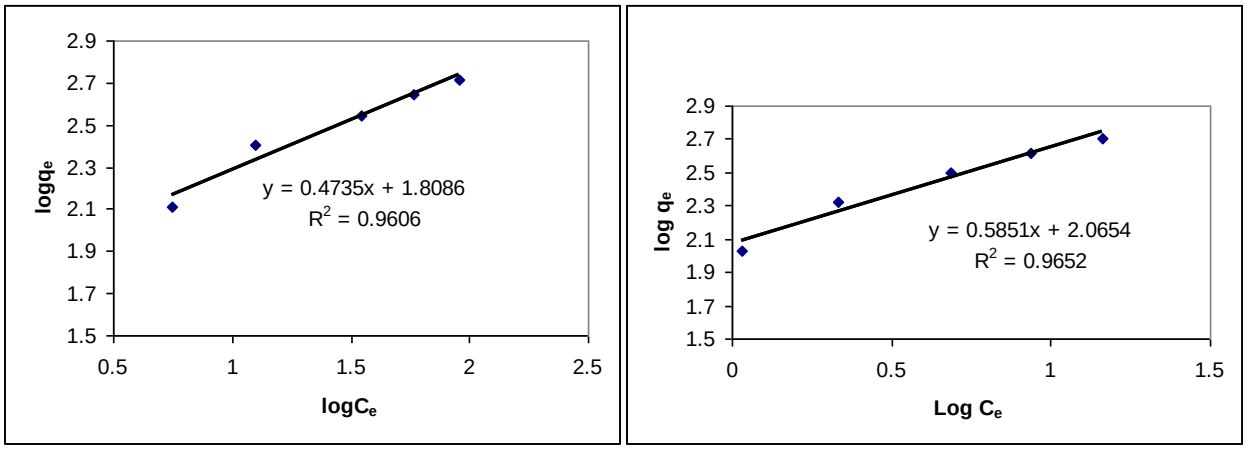
(a) BCG **(b) BCP**

Figure (6): Freundlich isotherm for two dyes adsorption by using the activated carbon prepared ACPA



(a) BCG **(b) BCP**

Figure (7): Freundlich isotherm for two dyes adsorption by using the activated carbon prepared ACPN



(a) BCG **(b) BCP**

Figure (8): Freundlich isotherm for two dyes adsorption by using the activated carbon prepared ACPAN

Table(12): The values of Freundlich constants(K_f , n) and the correlation coefficients which were got from the application on the experimental data for adsorption

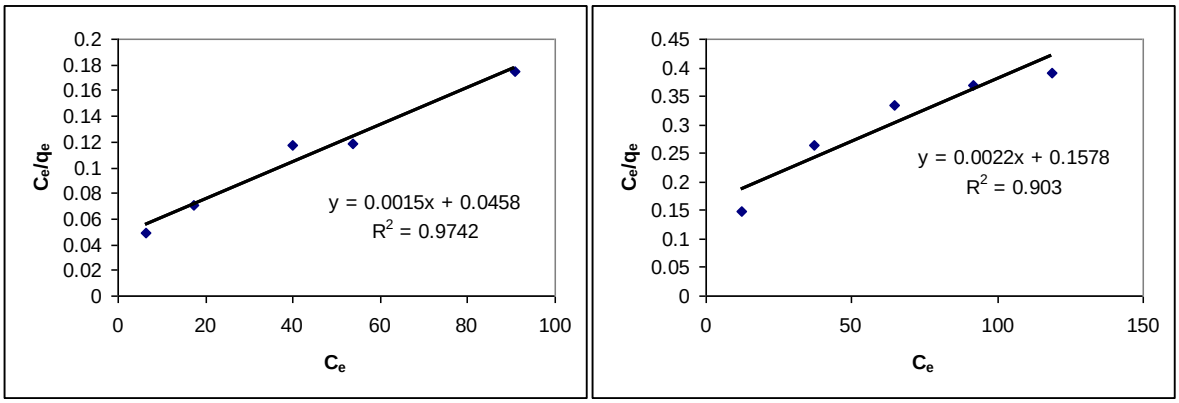
Type Activated carbon prepared	Dye	n	K_f	R^2
ACP	BCG	1.8760	49.750	0.9852
	BCP	1.7740	19.359	0.9912
ACPA	BCG	2.1663	64.135	0.9743
	BCP	1.7304	37.948	0.9702
ACPN	BCG	1.4291	39.463	0.9917
	BCP	1.6482	102.117	0.9778
ACPAN	BCG	2.1119	64.357	0.9606
	BCP	1.7091	116.251	0.9652

The results in the table(12) refer to Freundlich isotherm -equation which is suitable to the experimental data for the well studied system, it indicates that the values of correlation coefficient are near to one, whereas *n* value (in the range of 1-10) indicates that the adsorption- system is the preferable one (and is controlled by physical powers).

6.2: Langmuir isotherm

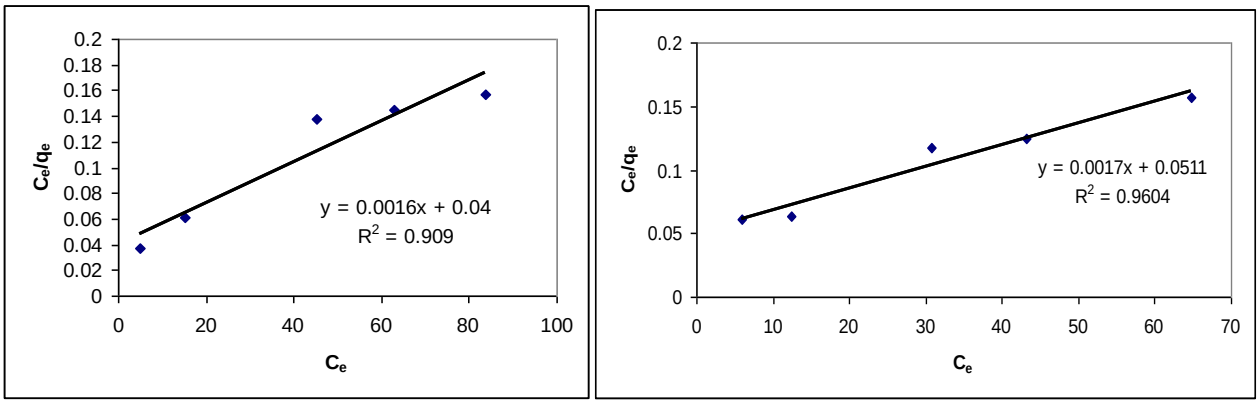
This sample of isotherms is important in describing and studying the mono-layer adsorption, it presupposes the homogeneity of energy on the surface of the adsorbent material at constant temperature. This gives the researcher information represents maximum capacity for adsorption (Q_{max}) for the adsorbent material as well as the strength of connection between the dye and adsorbent surface through the constant(b).

This sample was applied -as in the equation(13)- on the experimental data for two dyes adsorption through drawing the relation between C_e/q_e in opposite to C_e. The constants Q_{max} and b were calculated through the slop and straight lines section that were formed from the drawings respectively. The results got were listed in the table(13), they were represented graphically as in the following figures:



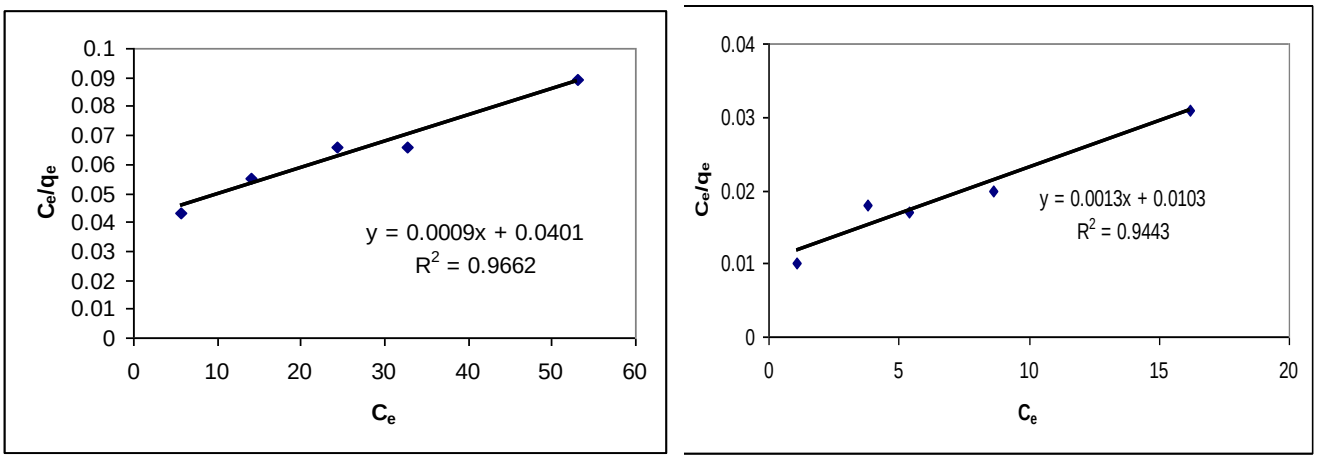
(a) BCG **(b) BCP**

Figure (9): Langmuir isotherm for adsorption of two dyes by using the activated carbon prepared ACP



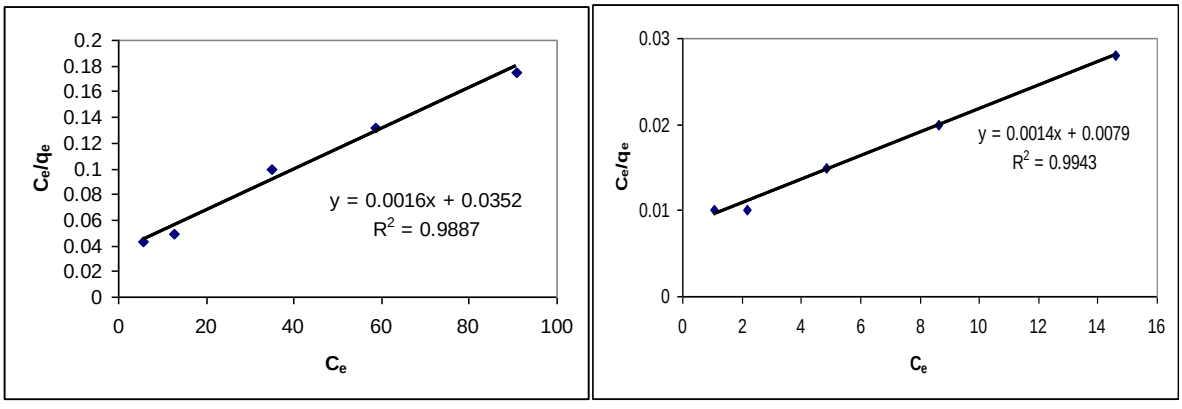
(a) BCG **(b) BCP**

Figure (10): Langmuir isotherm for adsorption of two dyes by using the activated carbon prepared ACPA



(a) BCG **(b) BCP**

Figure (11): Langmuir isotherm for adsorption of two dyes by using the activated carbon prepared ACPN



(a) BCG **(b) BCP**

Figure (12): Langmuir isotherm for adsorption of two dyes by using the activated carbon prepared ACPAN

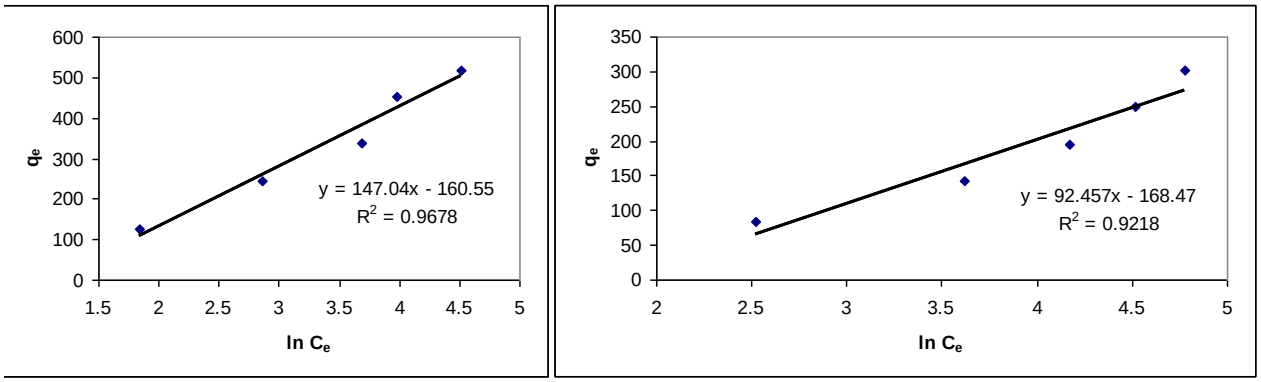
Table(13): The values of Langmuir constants(Q_{max}, b) as well as the correlation coefficients which were got by applying them on the experimental data for adsorption

Type Activated carbon prepared	Dye	Q(mg/g)	b(L/mg)	R^2
ACP	BCG	666.666	0.0327	0.9742
	BCP	454.545	0.0139	0.903
ACPA	BCG	625	0.0400	0.909
	BCP	588.235	0.0332	0.9604
ACPN	BCG	1111.111	0.0224	0.9662
	BCP	769.230	0.1262	0.9443
ACPAN	BCG	625	0.0454	0.9887
	BCP	714.285	0.1772	0.9943

6.3: Tempkin isotherm

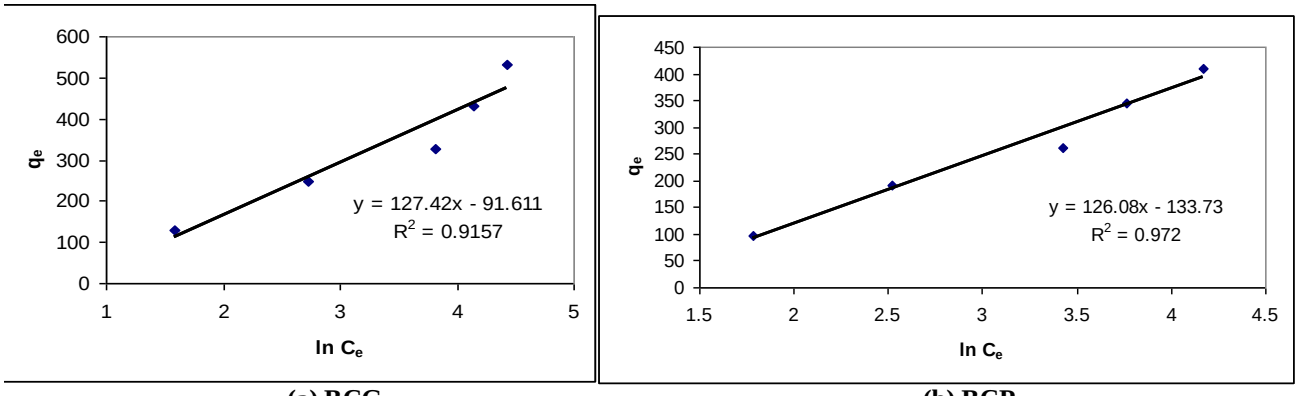
Tempkin isotherm was tested on the experimental data for adsorption system(dye-carbon) by using the (equation 14), through drawing the relation between q_e in opposite to $\ln C_e$ and the values of the constants B_T and K_T were calculated respectively from the slop and the straight lines section that were got.

The results which were got, listed in the table(14), they were represented graphically as it is illustrated in the following figures:



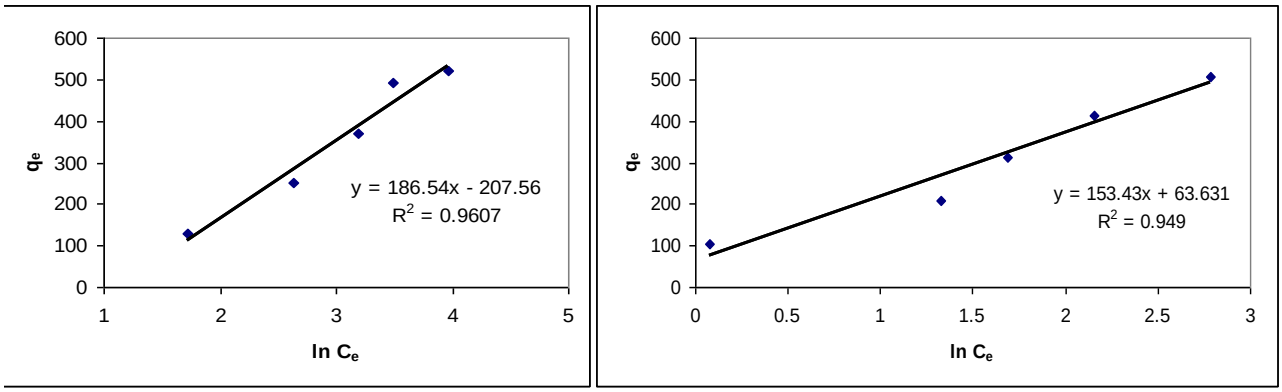
(a) BCG **(b) BCP**

Figure (13): Tempkin isotherm for adsorption of two dyes by using the activated carbon prepared ACP



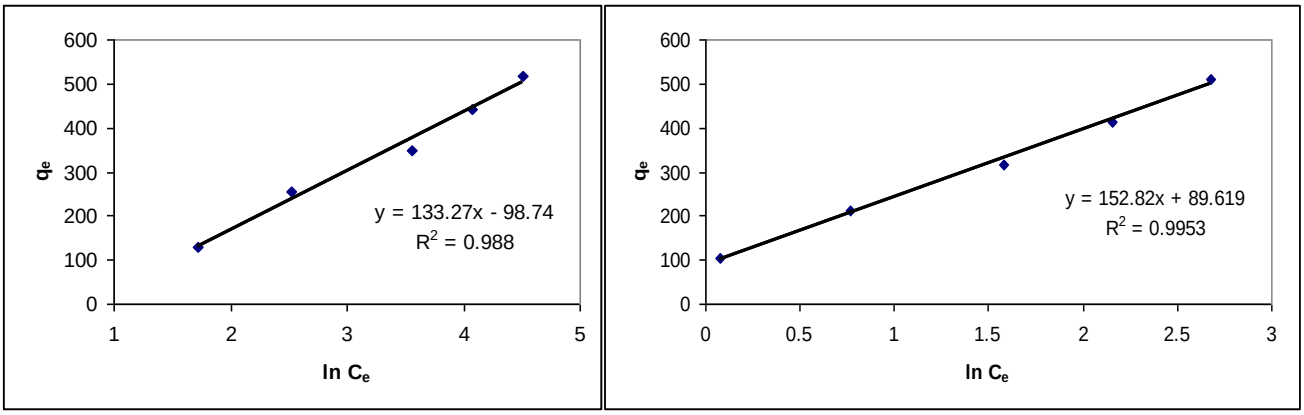
(a) BCG **(b) BCP**

Figure (14): Tempkin isotherm for adsorption of two dyes by using the activated carbon prepared ACPA



(a) BCG **(b) BCP**

Figure (15): Tempkin isotherm for adsorption of two dyes by using the activated carbon prepared ACPN



(a) BCG **(b) BCP**

Figure (16): Tempkin isotherm for adsorption of two dyes by using the activated carbon prepared ACPAN

Table(14): The values of Tempkin constants (B_T , K_T) and correlation coefficients which were got by their application on the experimental data for adsorption

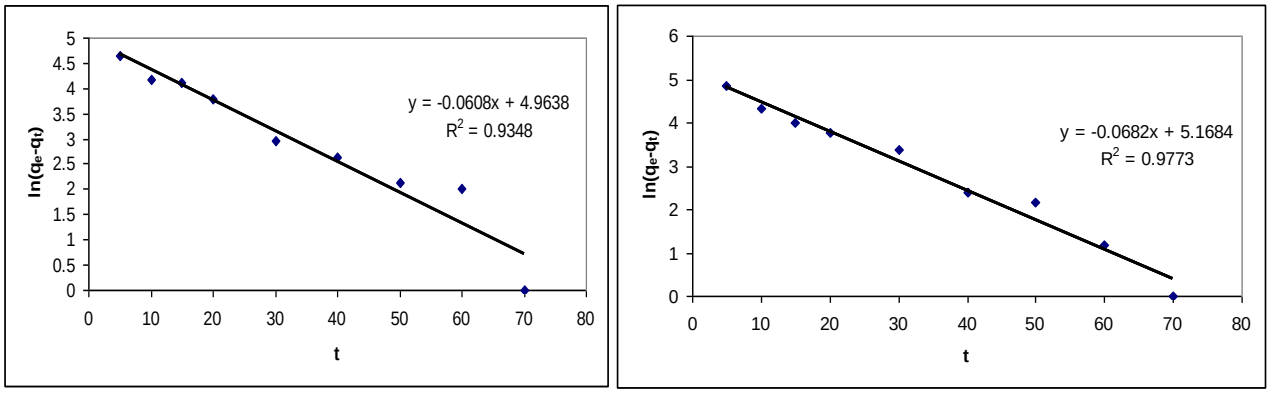
Type Activated carbon prepared	Dye	B_T	K_T	R^2
ACP	BCG	147.04	0.3356	0.9678
	BCP	92.457	0.1616	0.9218
ACPA	BCG	127.42	0.4872	0.9157
	BCP	126.08	0.3462	0.972
ACPN	BCG	186.54	0.3287	0.9607
	BCP	153.43	1.5128	0.949
ACPAN	BCG	133.27	0.4766	0.988
	BCP	152.82	1.7975	0.9953

Collectively, the results got by the study as for applying the three isotherm equations on the experimental data for the studied systems- adsorption showed that Freundlich isotherm model was more applicable on the got practical results than other models as far as this study is concerned.

7: Kinetic study of adsorption

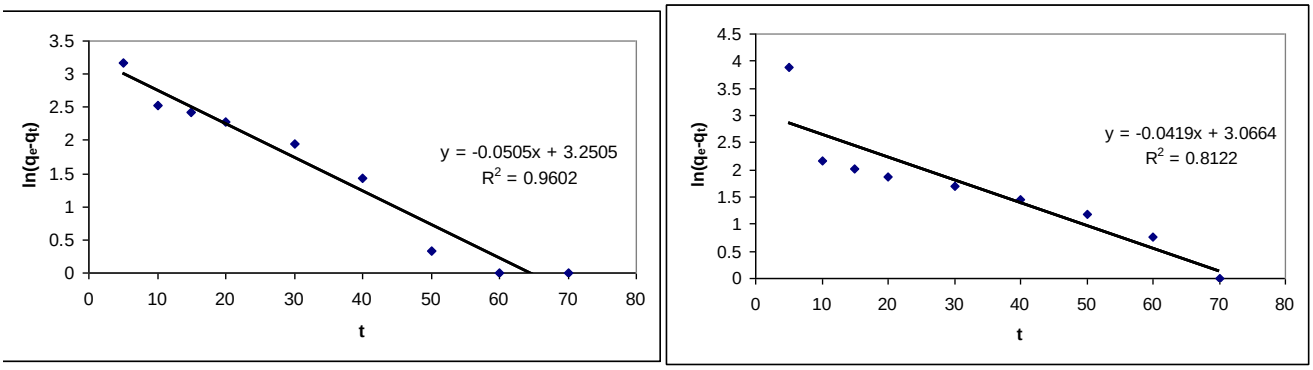
1: Pseudo first order equation

The pseudo first order equation sample (equation 15) which is so called Lagergren equation was applied to the experimental data for adsorption dyes under study through drawing the relation between $\ln(q_e\text{-}q_t)$ in opposite to the time(min) to have linear correlation of slop was about($-k_1$) and section $\ln q_e$ in which the constants k_1 and q_e can be calculated respectively. The final results got were listed in the table(15) and explained in the figures(17,18,19,20).



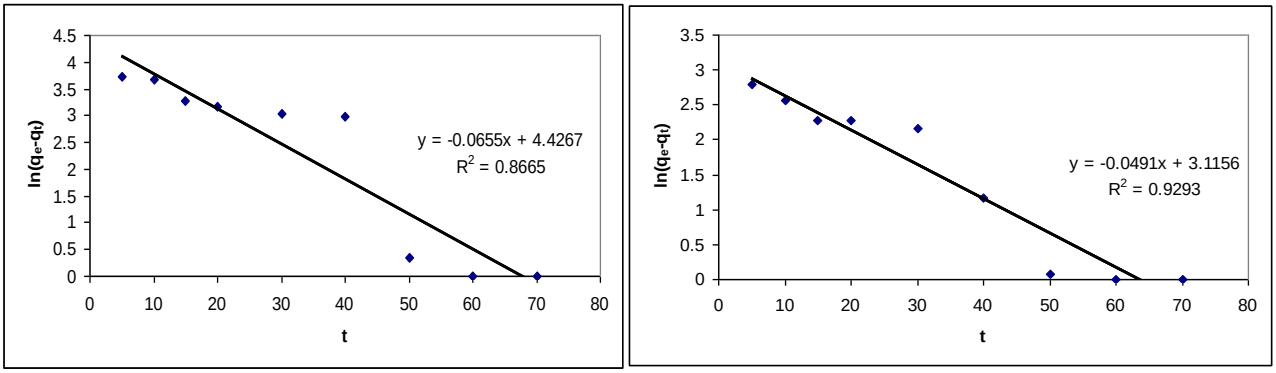
(a) BCG **(b) BCP**

Figure (17): The relation between $\ln(q_e - q_t)$ in opposite to the time(minute) for the two dyes by using the activated carbon prepared ACP



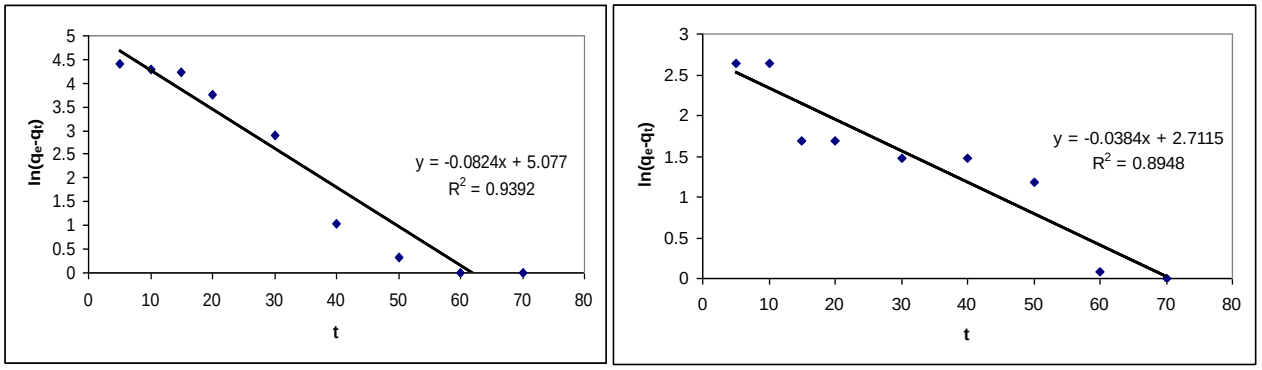
(a) BCG **(b) BCP**

Figure (18): The relation between $\ln(q_e - q_t)$ in opposite to the time(minute) for the two dyes by using the activated carbon prepared ACPA



(a) BCG **(b) BCP**

Figure (19): The relation between $\ln(q_e - q_t)$ in opposite to the time(minute) for the two dyes by using the activated carbon prepared ACPN



(a) BCG **(b) BCP**

Figure (20): The relation between $\ln(q_e - q_t)$ in opposite to the time(minute) for the two dyes by using the activated carbon prepared ACPAN

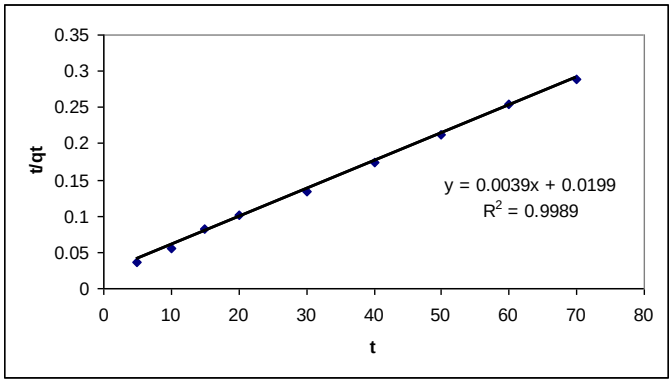
Table(15): the values of velocity constants and the theoretical-practical adsorption capacity for the pseudo first order; the quantity of the activated carbon: 0.01g at 25C°

Type Activated carbon prepared	Dye	q_e(exp)mg/g	q_e(calc)mg/g	k_1(min^{-1})	R^2
ACP	BCG	242.908	143.136	0.0608	0.9348
	BCP	140.464	175.633	0.0682	0.9773
ACPA	BCG	245.7	25.803	0.0505	0.9602
	BCP	181.522	21.464	0.0419	0.8122
ACPN	BCG	251.284	83.654	0.0655	0.8665
	BCP	208.534	22.546	0.0491	0.9293
ACPAN	BCG	252.68	160.292	0.0824	0.9392
	BCP	211.776	15.051	0.0384	0.8948

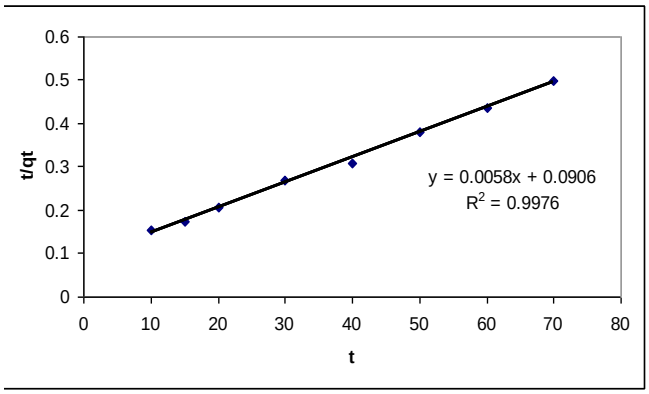
2: Pseudo-second order equation

The pseudo second order equation-model (equation 16) was applied on the experimental data for adsorption dyes on the activated carbon through drawing the relation between t/q_t in opposite to the time(min).

The values of the slop and straight lines section got by the graphic representation were used to calculate the values of velocity constant (k_2) (g.mg^{-1}.min^{-1}) and the adsorption capacity at the equilibrium q_e (mg/g) respectively. The results got are explained in the table(16) and drawn graphically in the figures (21,22, 23, 24,).

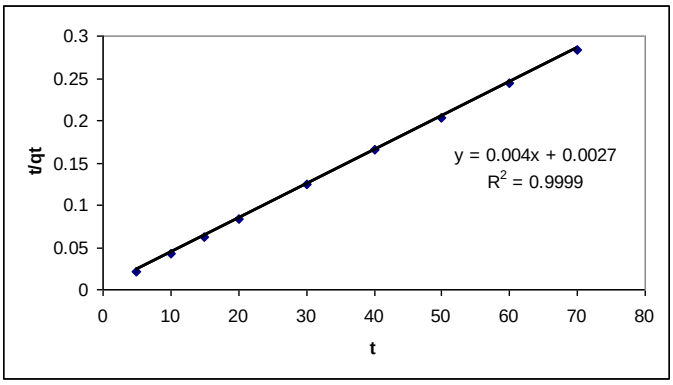


(a) BCG

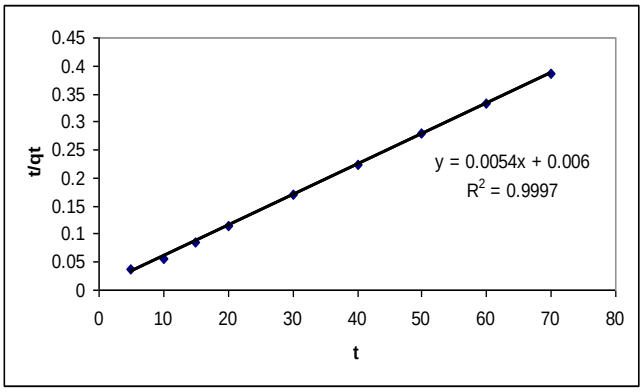


(b) BCP

Figure (21): The relation between t/q_t in opposite to the time(minute) for two dyes by using the activated carbon prepared ACP

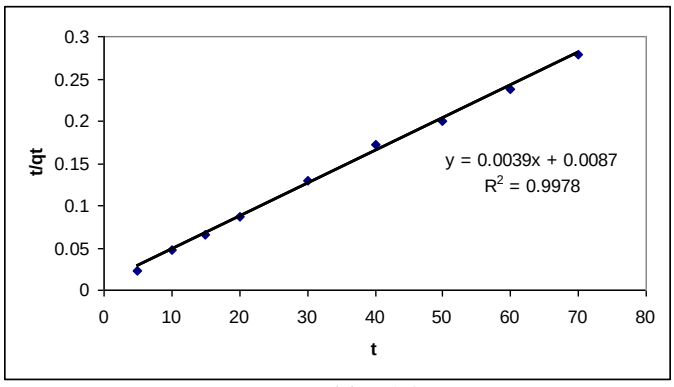


(a) BCG

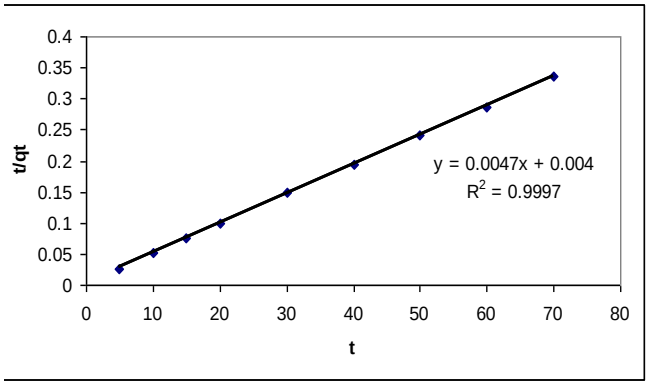


(b) BCP

Figure (22): The relation between t/q_t in opposite to the time(minute) for two dyes by using the activated carbon prepared ACPA

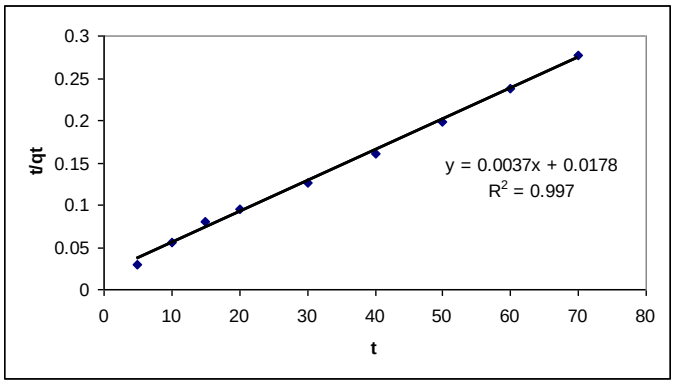


(a) BCG

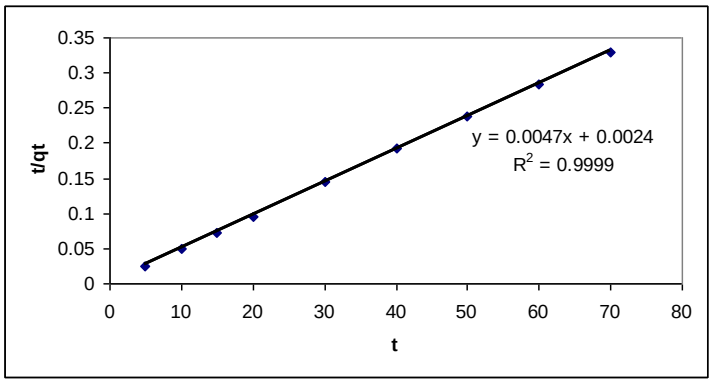


(b) BCP

Figure (23): The relation between t/q_t in opposite to the time(minute) for two dyes by using the activated carbon prepared ACPN



(a) BCG



(b) BCP

Figure (24): The relation between t/q_t in opposite to the time(minute) for two dyes by using the activated carbon prepared ACPAN

Table(16): The values of the velocity constants and the theoretical-practical adsorption capacity of the pseudo second order; the quantity of the activated carbon: 0.01g at 25C°

Type Activated carbon prepared	Dye	q_e(exp)mg/g	q_e(calc)mg/g	k_2 ($g.mg^{-1}.min^{-1}$)	h ($mg.g^{-1}.min^{-1}$)	R^2
ACP	BCG	242.908	256.410	0.00076	44.843	0.9989
	BCP	140.464	172.413	0.00037	7.300	0.9976
ACPA	BCG	245.7	250	0.00590	356.174	0.9999
	BCP	181.522	185.185	0.00480	158.161	0.9997
ACPN	BCG	251.284	256.410	0.00174	109.869	0.9978
	BCP	208.534	212.765	0.00552	240.045	0.9997
ACPAN	BCG	252.68	270.270	0.00076	48.523	0.997
	BCP	211.776	212.765	0.00920	412.611	0.9999

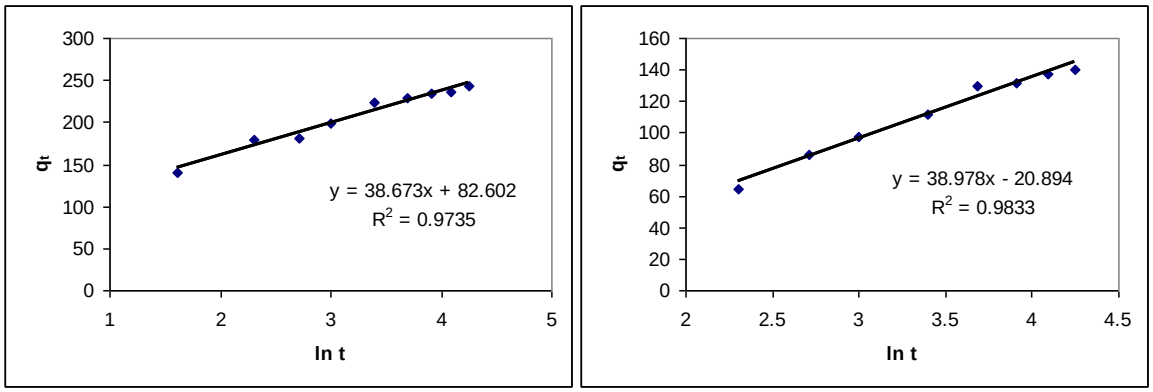
Looking carefully at the results listed in the two tables(15 and 16), we have found that the other way round of the pseudo first order equation. An excellent linear relation was given by applying pseudo second order equation model. This was indicated by the values of correlation coefficients (R^2) which were about (0.997 – 0.9999), furthermore, the capacity adsorption values calculated from the straight lines slop were more harmonized with the adsorption-experimental values of the pseudo second order kinetic equation model with regard to the systems under study. We can find that capacity adsorption was appropriate inversely with the velocity-constant of the reaction(adsorption) as for pseudo second order. This differentiation can be accounted for through calculating the primary velocity for the adsorption which discriminates this kind of this model of kinetic equations through the following equation[28].

$$h = k_2 (q_e)^2 \text{.....(20)}$$

h value represents a constant ($mg.g^{-1}.min^{-1}$), so called the primary adsorption velocity-average. The results indicate that as soon as the primary velocity(adsorption efficiency) for the dye is large, the carbon surface would be occupied by molecules- dye more quickly, this leads to lowness of adsorption- speed more largely, thus, this is in accordance to what has been noticed in the course of studying concentration effect and time on the adsorption- efficiency.

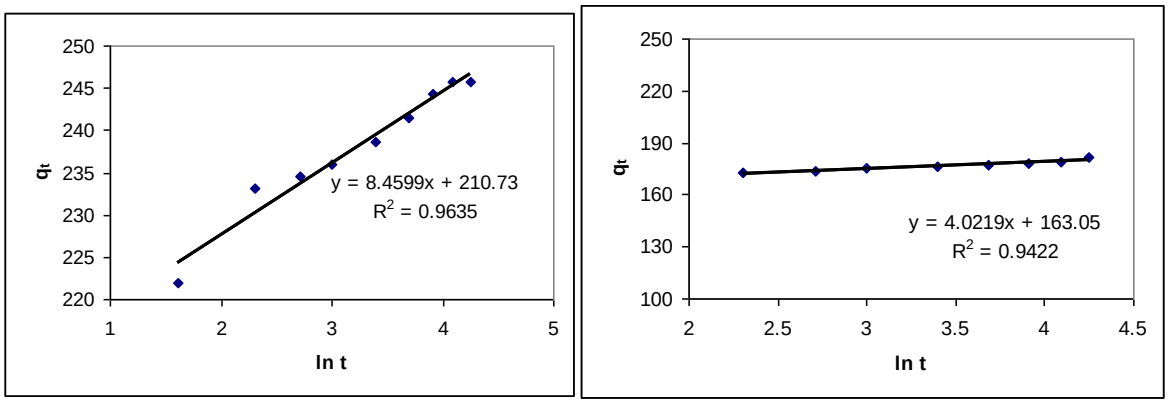
3: Elovich kinetic equation

The Elovich kinetic equation (equation 17) was applied on the experimental data for the adsorption of dyes under study, on the activated carbon. The results got were listed in the table(17) and they were represented graphically by the shown drawings (25,26,27,28).



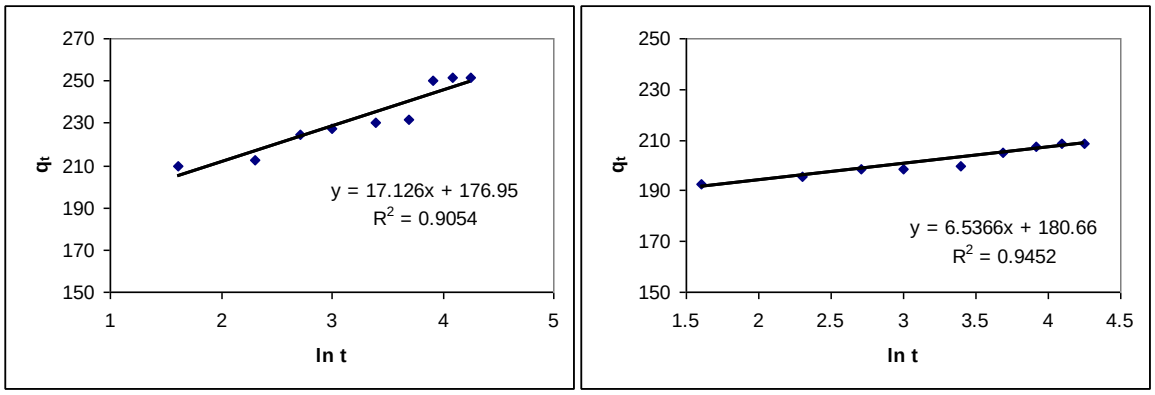
(a) BCG **(b) BCP**

Figure (25): The relation between q_t in opposite to lnt for the two dyes by using the activated carbon prepared ACP



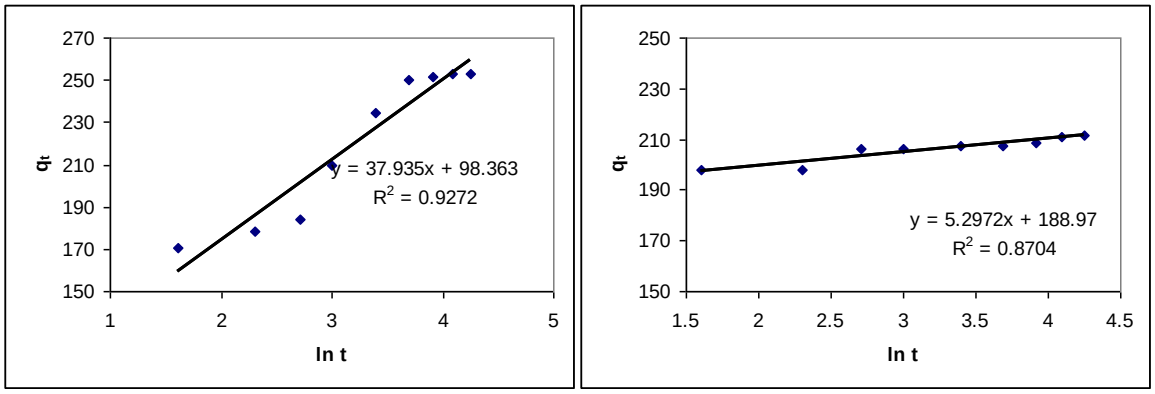
(a) BCG **(b) BCP**

Figure (26): The relation between q_t in opposite to lnt for the two dyes by using the activated carbon prepared ACPA



(a) BCG **(b) BCP**

Figure (27): The relation between q_t in opposite to lnt for the two dyes by using the activated carbon prepared ACPN



(a) BCG **(b) BCP**

Figure (28): The relation between q_t in opposite to lnt for the two dyes by using the activated carbon prepared ACPAN

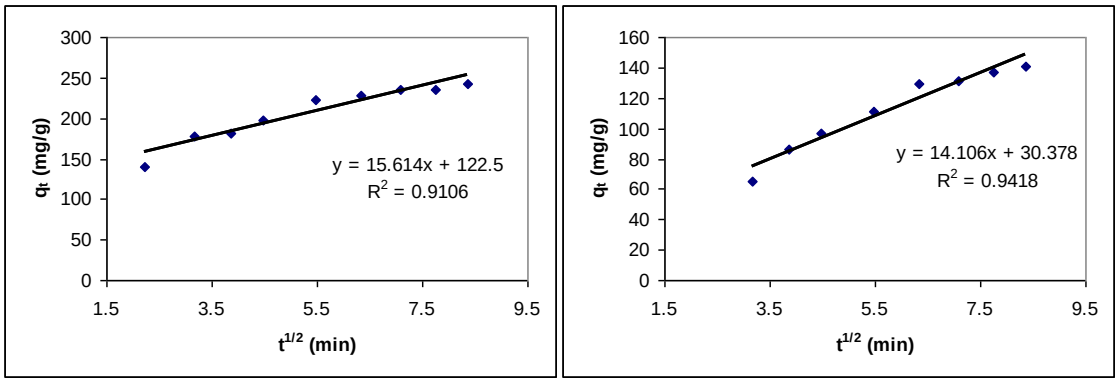
Table(17): The values of Elovich constants (α, β) and the correlation coefficients which were got by applying them on the experimental data for adsorption, the quantity of the activated carbon: 0.01g and at 25C°

Type Activated carbon prepared	Dye	Conc.(mg/L)	$(g.mg^{-1})\,\beta$	$(mg.g^{-1}.min^{-1})\,\alpha$	R^2
ACP	BCG	139.602	0.0258	328.028	0.9735
	BCP	108.048	0.0256	22.851	0.9833
ACPA	BCG	139.602	0.1182	5.5634E11	0.9635
	BCP	108.048	0.2486	1.6256E18	0.9422
ACPN	BCG	139.602	0.0583	5.26705347 E5	0.9054
	BCP	108.048	0.1529	6.5874857 E12	0.9452
ACPAN	BCG	139.602	0.0263	508.325	0.9272
	BCP	108.048	0.1887	1.6483E16	0.8704

The results got by applying Elovich equation and listed in the table(17) that the primary velocity(α) for dye-correlation BCG was much bigger than the dye BCP, this might be because of the sterically hindered formed by the substitution of the two bromine atoms in the dye-structure of BCG, in two groups- methyl within the dye: BCP, the structure of the two dyes was similar, except that this difference, perhaps, might be a general reason for all of what has been noticed of distinctions as for the efficiency of the two mentioned dyes adsorption.

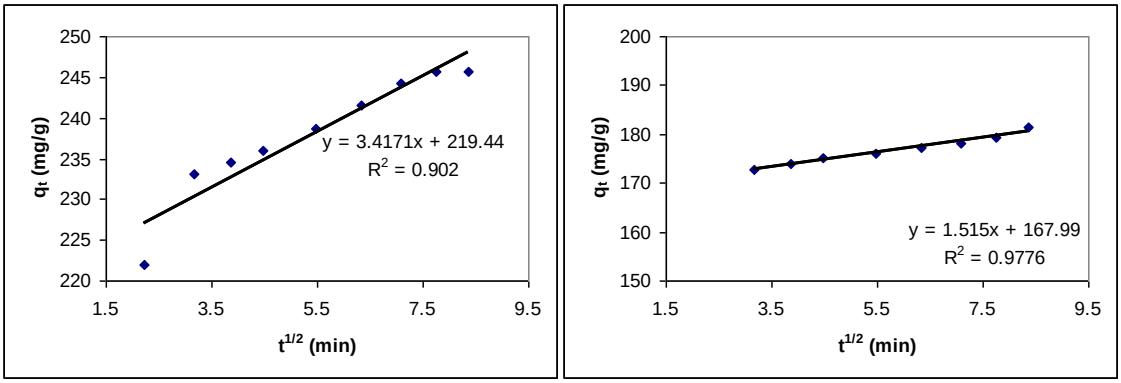
4: The intra particle diffusion equation

According to the intra particle diffusion equation, the dyes under study will be transform from their aqueous solution to the activated carbon surface, then, they will intervene to the pores found on the carbon surface by the intra particle diffusion, accordingly, the adsorption process will go through more than one speed and its activated energy differentiate in harmony with each passing phase, thereby, the intra particle diffusion model should be the fourth kinetic model which should be used in studying the determining step for the velocity of selected dyes adsorption on the activated carbon. This can be done through the (equation 18). The results got listed in the table(18) and they were represented graphically by the showing draw in the figures(29,30,31, 32,).



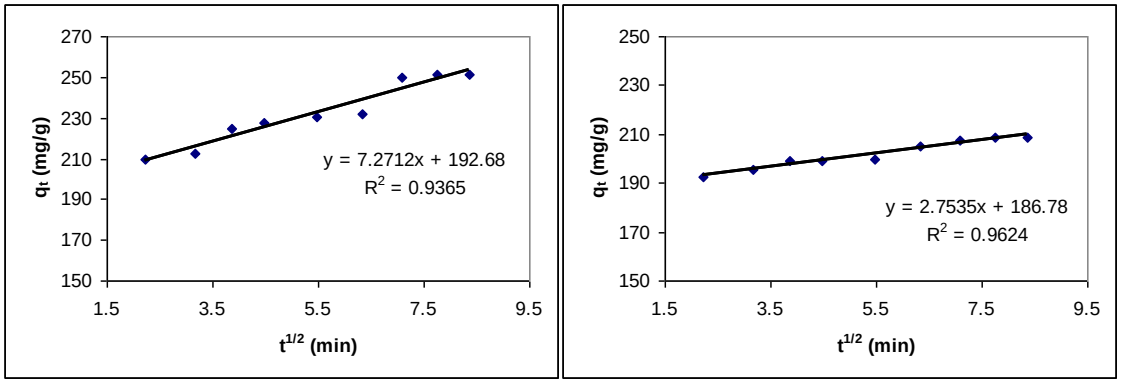
(a) BCG **(b) BCP**

Figure (29): The relation between q_t in opposite to $t^{1/2}$ for the two dyes by using the activated carbon prepared ACP



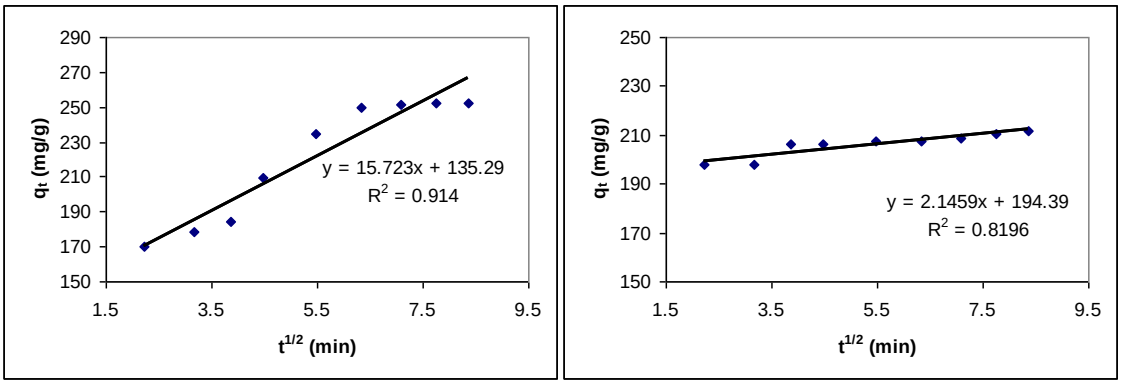
(a) BCG **(b) BCP**

Figure (30): The relation between q_t in opposite to $t^{1/2}$ for the two dyes by using the activated carbon prepared ACPA



(a) BCG **(b) BCP**

Figure (31): The relation between q_t in opposite to $t^{1/2}$ for the two dyes by using the activated carbon prepared ACPN



(a) BCG **(b) BCP**

Figure (32): The relation between q_t in opposite to $t^{1/2}$ for the two dyes by using the activated carbon prepared ACPAN

Table(18):The values of intra particle diffusion constants (k_{diff} , C) and correlation coefficients which were got by applying them on the experimental data for adsorption, the quantity of the activated carbon:0.01g and at 25C°

Type Activated carbon prepared	Dye	C_i(mg/L)	K_{diff}(mg.g^{-1}.min$^{-1/2}$)	C(mg/g)	R^2
ACP	BCG	139.602	15.614	122.5	0.9106
	BCP	108.048	14.106	30.378	0.9418
ACPA	BCG	139.602	3.4171	219.44	0.902
	BCP	108.048	1.515	167.99	0.9776
ACPN	BCG	139.602	7.2712	192.68	0.9365
	BCP	108.048	2.7535	186.78	0.9624
ACPAN	BCG	139.602	15.723	135.29	0.914
	BCP	108.048	2.1459	194.39	0.8196

According to the got results in the table (18) and from the figures seen (29,30,31,32), The intra particle diffusion-mechanism will form the only mechanism governing the adsorption process, when the draw gives the relation between q_t opposite to $t^{1/2}$ as a straight line through the radix point. Perhaps, this action does not happen, so one can conclude that the intra particle diffusion process plays a vital role in removing the dye from its aqueous solutions by using the activated carbon prepared, but the tentative results suggest that they are not the only step that runs and controls the dye adsorption[37,38].

Table(19): A comparison between the adsorption capability on the kinds of activated carbon prepared and the commercial activated carbon as for two dyes from their aqueous solutions

Sample	Type Activated carbon prepared	pH V:V Ethanol : Distillation Water %50	% Adsorption Dye BCG pH=3.81 V:V Ethanol : Distillation Water %50	% Adsorption Dye BCP pH=5.22 V:V Ethanol : Distillation Water %50
5	ACP	5.23	87.00	65.00
11	ACPA	8.00	88.00	84.00
16	ACPN	8.63	90.00	96.50
21	ACPAN	8.72	90.50	98.00
B.D.H*		4.36	79.50	55.00

We can notice of the results shown in the above table, that the capability related to the kinds of activated carbon prepared for adsorption two dyes of their aqueous solutions differentiate by depending on the chemical structure for two dyes, but generally, they are higher than the capability of the commercial activated carbon for adsorption.

CONCLUSIONS

Experimentally, it was found that the activated carbon prepared by pomegranate peels as a raw material having high adsorptive capacity with respect to adsorbing and removing the dyes BCG and BCP from their aqueous solutions; the effective factors on the adsorption- efficiency were studied, it was shown that the adsorption-efficiency increased and its capacity decreased in the course of increasing the adsorbent material. The adsorption would be very quick in the first minutes, then, it would slow down reaching the equilibrium state through 60-70 min. for the dye under discussion. Freundlich isotherm model gave a better application on the studied system, and in less degree, Langmuir & Tempkin isotherms in the course of the applying on the experimental adsorption data. The values of the thermodynamic functions indicated that the studied dyes- adsorption on the activated carbon prepared-samples was an exothermic process having physical nature and occurred spontaneously. The results of the kinetic study showed that the adsorption system was in accordance to the pseudo second order equation, also, it was noticed that applying Elovich equation model where the primary velocity for the adsorption process was compatible with what was noticed and got during the application of pseudo second order equation. Finally, the intra particle diffusion model played a vital role in removing the dye from its aqueous solution by using the activated carbon during the application.

REFERENCES

[1]. Al-Dobouni I. A.,(1991),"Introduction of Petrochemicals", Print1, University of Mosul, PP. 307-318.
[2]. Green wood N., Earnshaw A.,(1986) "Chemistry of Elements", McGraw-Hill, New York, USA, pp. 296-304.
[3]. Qasim L. E.,(1991),"Product Activated Carbon from Vegetarianism sources ", MSc. Thesis, University of Mosul.
[4]. Yamaguchi T. ,Sato Y.,(1993), "Preparation of activated carbon from thioliguine with alkali",Nippon kagoku kaishi,ISS.3,271-277.
[5]. Rahman I.A., saad B.,(2003),"Utilization of Guava seeds as a source of Activated Carbon for Removal of Methylene Blue from Aqueous Solution", Malaysian Journal of Chemistry, Vol. 5,No. 1, pp. 8-14.
[6]. AL Ghannam K.A., Aweed K.A., Hamdoon A.A.,(2004),"Preparation of activated from Morus nigra by chemical treatment", National Journal of Chemistry, Vol.13,pp.26-33.
[7]. Aweed K.A.,(2005),"Production of activated carbon from some agricultural wastes by chemical treatment", National J. of Chemistry,Vol.17, pp. 32-54.
[8]. AL-Baidhany J.H., AL-Tufaily M.A.,AL-Taliby W.H., (2009),"Adsorption of Methylene Blue Dye onto Different Types of Adsorbent Beds" Babylon University/ College of Engineering.
[9]. Ananthabaskaran T. ,(2011)," Adsorptive Removal of Methylene Blue onto $ZnCL_2$ Activated Carbon from Wood Apple Outer Shell : Kinetics and Equilibrium studies", E-Journal of Chemistry,8(4), 1696-1707.
[10]. Dakheel A. B.,(2012),"Preparation of A Charcoal from Pine Wood Via Chemical Treatment", Tikrit Journal of Pure Science, Vol. 17, No. 3,PP. 153-155.
[11]. Dash B., (2010),"Competitive Adsorption of dyes (Congo red , Methylene blue, Malachite green) on Activated Carbon", National Institute of Technology, Rourkelq.
[12]. Venckatesh R., Amudha T., Sivaraj R., Chandramohan M., and Jambulingam M., (2010), " Kinetics and Equilibrium Studies of Adsorption of Direct Red-28 on to punica granatum carbon", International Journal of Engineering Science and Technology Vol. 2,No.6, pp. 2040-2050.
[13]. Mane R.S., Bhusari V.N.,(2012),"Removal of Colour (dyes) from textile effluent by adsorption using Orange and Banana peel",International Journal of Engineering Research and Applications,Vol. 2, Issue. 3, pp. 1997-2004.
[14]. AL-Hyali E.A.S,, Abraheem M.A., Azeez A.A.,(2013),"Comparison Study of the Adsorption of Copper Ions By Activated Carbon and Alocally Collected Bentonite", J.Edu & Sci., Vol.26, No.2.
[15]. Salman J.M., (2013), "Preparation of Mesoporous-Activated Carbon from Branches of Pomegranate Trees:Optimization on Removed of Methylene Blue Using Response Surface Methodology", Journal of chemistry,Vol.2013,pp.6.
[16]. Radaei E., Moghaddam M.R., Arami M., (2013),"Adsorption of reactive blue 19 on to activated carbon prepared from pomegranate residual by phosphoric acid activation : Kinetic , Isotherm and Thermodynamic studies", J. Prog. Color, Colorants, Coatings.
[17]. Moghadam M. R., Nasirizadeh N., Dashti Z., and Babanezhad E., (2013), "Removal of Fe(II) from aqueous solution using pomegranate peel carbon: equilibrium and kinetic studies", International Journal of Industrial Chemistry (IJIC), 4:19
[18]. AWWA Standard for Granular activated carbon,(1974),B604-74,Sec.7,Approved by J.theAmerican water works association board of directors on Jan.28.

[19]. ASTMD2854-70,"Standard Test Method for Apparent Density Activated Carbon".
[20]. ASTMD2866-70,(1916) " Total Ash content of Activated Carbon", Extracts were Reprinted with Permission from the Annual Book of ASTM Standard Copyright ASTM Race Street.
[21]. ISO,5.62,(1981),"Determination of Volatile Matter Content of Hard Coal and Coke", the Full Text can be Obtained from ISO Central Secretariat Cose postable 5G,CH-1211:Genra 20 or from any ISO Member.
[22]. El Nemr A.,(2007), " Pomegranate husk as an adsorbent in the removal of toxic chromium from waste water", Chemistry Ecology , 23(5), 409-425.
[23]. AL-Ghouti M.A., KhraishehM.A.M., Allen S.J .,and Ahmed M.N., (2003), "The removal of dyes from textile waste water : a study of physical characteristics and adsorption mechanisms of diatomaceous earth", J.Enu. Manag.69.230-237.
[24]. Abdelwahab O., (2007), " Kinetic and isotherm studies of copper (II) removal from waste water using various adsorbents ", Egyptian J. Aqu. Res., 33, 136.
[25]. Lagergren S.,(1898), " About theory of SO-Called adsorption soluble substances" , dersogenannten adsorption geloster stoffe kungliga svenska vetenska psalka demiens handling ar, 24,1-39.
[26]. Dima A.A., (2008), " Adsorptive removal of reactive azo dyes using industrial residue" , M.Sc . Thesis, University of Addis Ababa.
[27]. Ho Y.S., Mckay G., (1998), " Sorption of dye from aqueous solution by peat" , Chem.Eng.J.,70,115-124.
[28]. Ho Y.S., Mckay G., (2000), " The kinetics of sorption of divalent metal ions onto sphagnum moss peat " , water Res., Vol. 34,No.3, pp.735-742.
[29]. Chien S.H. , Clayton W. R., (1980), " Application of Elovich equation to the kinetics of phosphate release and sorption on soils", soil sci, Soc. Am.J.,44,265-268.
[30]. Bulut Y., Gozubenli N., Aydm H., (2007), " Equilibrium and kinetic studies of adsorption of direct blue 71 from aqueous solution by wheat shells" , J.Hazard. Mater., 144,303-305.
[31]. Ramadhan O.M., Rigibi M.A., (2000), " Activated Carbon by Modified Carbonization" , Vol.46,J.Sci.Edu.
[32]. Teng H.S., Weng T.S., (2001), " Transformation of mesophase pitch in to different carbons by heat treatment and KOH etching" , J.Microporous Mesoporous Mat., Vol.50, No.1, pp.53-60.
[33]. Mahajan Omp ., Walker P.L., (1979), " Effect of inorganic matter removed from coals and chars on their surface areas" , Fuel, Vol. (58), pp.333-3337.
[34]. Inbaraj B.S., Chien J.T., HO G.H., Yang J., and Chen B.H., (2006), "Equilibrium and kinetic studies on sorption of basic dyes by anatural biopolymer poly (glutamic acid) .J.Biochemistry and Eny., 31,209-211.
[35]. Malik R., Ramteke D.S., Wate S.,(2006)," Adsorption of malachite green on groundnut shell waste based powderd activated carbon",J.Was.Manag., 27, 1-8.
[36]. Reddy S.S., Kotaiah B., Reddy N.S.P., and Velu M., (2006), " The removal of composite reactive dye from dyeing unit effluent using sewage sludge derived from activated carbon" , Turk.J.Eng.Env.Sci., 30,370.
[37]. Rajoriya R.K., Prasad B., Mishra I.M., and Wasewar K.L., (2007) , " Kinetics, equilibrium , and thermodynamics", Chem.. Biochem. Eng.Q.,21,221-224.
[38]. Wu C.H., (2007) , "Adsorption of reactive dyes onto carbon nanotubes: Equilibrium , Kinetics and thermodynamics" , J.Hazard.Mater.144,96-98.